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SYMMETRICAL DEFORMATION OF A THIN TOROIDAL SHELL OF ELLIPTICAL CROSS-SECTION

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ABSTRACT

This paper presents an approximate computation method of stress and strain components in a thin-walled toroidal elastic shell of elliptical cross-section, limited by two parallels $\theta = \theta_1, \theta = \theta_2$ (Figure 1), and loaded arbitrarily but symmetrically with respect to the axis of revolution. Making use of E. Meissner's variables and neglecting small terms, the problem is reduced to the determination of a complex function $X(\theta)$ satisfying a differential equation with suitable boundary conditions. Applying asymptotic methods of integration, the solution in closed form is found, the desired function X being tabulated or expressed by means of simple asymptotic formulas.

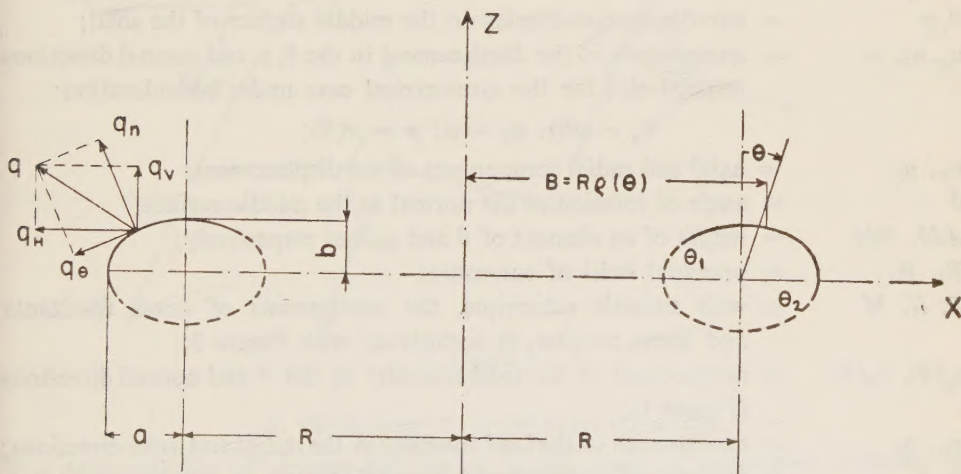


Figure 1

1. INTRODUCTION

The problem of strength of thin-walled shells of revolution loaded symmetrically has been solved in principle. Recently the efforts of investigators have been aimed towards the simplification of computational methods and examination of the accuracy of the existing methods.

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The problem of the toroidal shell is especially difficult since the product of the principal curvatures of its middle surface changes in sign from positive through zero to negative.

The solution of adequate differential equations is therefore rather complicated, and the approximate "engineering" methods of calculation based on the well-known theory of Geckeler lead to absurd results.

The first solution of the problem of the toroidal shell of circular cross-section was published, as far as known to the author, by H. Wissler in 1916, but quite accurate and much simpler calculation methods have recently been worked out nearly simultaneously by R.A. Clark² and E. F. Zenova and V. V. Novoshilov⁵.

The author has proposed in an earlier paper⁴ that these shells be calculated by a combined method, using Zenova and Novoshilov's solution for the homogeneous problem (general integral) and that of Clark for the calculation of the particular integral.

In the present paper, this asymptotic method of calculation is extended to toroidal shells of elliptical cross-section.

2. NOMENCLATURE

θ, φ	= curvilinear coordinates on the middle surface of the shell;
u_θ, u_φ, w	= components of the displacement in the θ, φ and normal directions respectively; for the symmetrical case under consideration: $u_\theta = u(\theta); u_\varphi = 0; w = w(\theta);$
u_V, u_H	= axial and radial components of the displacement;
θ	= angle of rotation of the normal to the middle surface;
$Ad\theta, Bd\varphi$	= length of an element of θ and φ lines respectively;
R_1, R_2	= principal radii of curvature;
T, N, M	= with suitable subscripts, the components of stress resultants and stress couples, in accordance with Figure 2;
$q_\theta(\theta), q_n(\theta)$	= components of the load intensity in the θ and normal directions (Figure 1);
q_H, q_V	= components of the load intensity in the radial and axial directions;
E, ν	= modulus of elasticity and Poisson's ratio;
δ	= thickness of the shell.
D	= $\frac{E\delta^3}{12(1-\nu^2)}$, flexural rigidity of the shell;
a, b	= semi-axes of the elliptical cross-section (Figure 1);
R	= radius of the axis of the shell;
λ	= $\frac{a}{R}$;

$$e = \frac{a^2 - b^2}{a^2} \geq 0$$

$$c = \frac{\delta}{\sqrt{12(1 - \nu^2)}}$$

$$2k^2 = \frac{ab}{Rc} = \sqrt{12(1 - \nu^2)} \frac{ab}{R\delta} \gg 1.$$

The prime denotes differentiation with respect to θ .

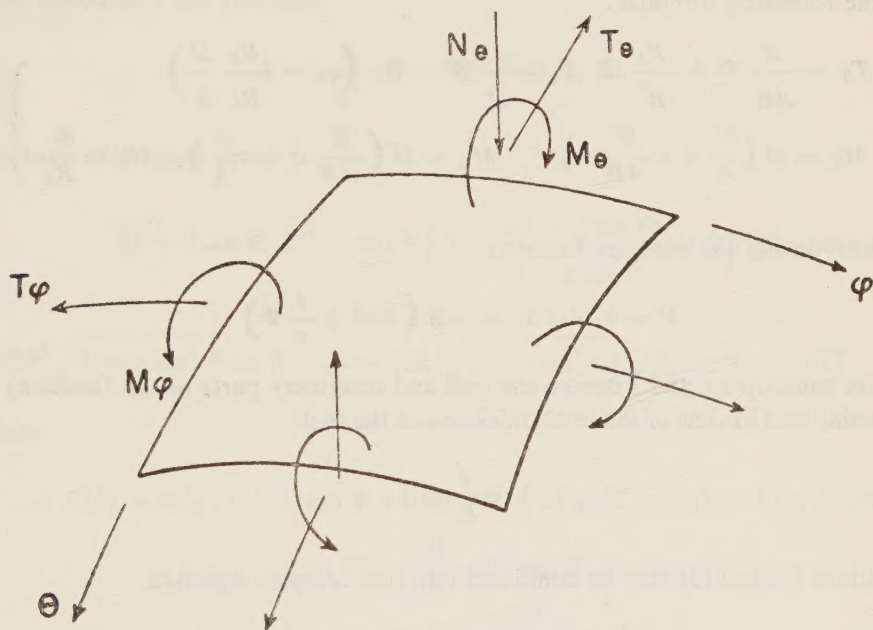


Figure 2

3. DEVELOPMENT OF THE BASIC EQUATION

The determination of stresses and strains in any shell of revolution subjected to a symmetrical load reduces to integration of the following two differential equations:

$$L(\vartheta) + \nu \left(\frac{B'}{A} \right)' \vartheta - \frac{BA}{R_2} \frac{1}{D} \Phi = 0 \quad (1)$$

$$L(\Phi) - \nu \left(\frac{B'}{A} \right)' \Phi + \frac{BA}{R_2} E \delta \vartheta = F(\theta) \quad (2)$$

where

$$L(\) = \frac{B}{A} (\)'' + \left(\frac{B}{A} \right)' (\)' - \frac{(B')^2}{AB} (\) \quad (3)$$

$$F(\theta) = -B \left\{ \left[R_2 q_n + \frac{R_2}{B^2} \left(1 - \frac{R_2}{R_1} \right) \Omega \right]' + A(1 + \nu) q_\theta \right\} \quad (4)$$

$$\Omega = \int_{\theta_1}^{\theta} \left(B B' q_n - \frac{AB^2}{R_2} q_\theta \right) d\theta + C_Q \quad (5)$$

C_Q = constant of integration.

The stress resultants and stress couples are related to Meissner's functions Φ , ϑ by the following formulas:

$$\left. \begin{aligned} T_\theta &= \frac{B'}{AB} \Phi + \frac{R_2}{B^2} \Omega, \quad T_\varphi = \frac{1}{A} \Phi' + R_2 \left(q_n - \frac{R_2}{R_1} \frac{\Omega}{B^2} \right) \\ M_\theta &= D \left(\frac{\vartheta'}{A} + \nu \frac{B'}{AB} \vartheta \right), \quad M_\varphi = D \left(\frac{B'}{AB} \vartheta + \nu \frac{\vartheta'}{A} \right), \quad N_\theta = \frac{\Phi}{R_2} \end{aligned} \right\} \quad (6)$$

By introducing the complex function

$$V = V_r + i V_i = -B \left(E \delta \vartheta + \frac{i}{c} \Phi \right) \quad (7)$$

(where subscripts r and i denote the real and imaginary parts of the function) and assuming that in view of the small thickness of the shell

$$1 + \frac{c}{R_1} \approx 1, \quad (8)$$

equations (1) and (2) may be combined into one complex equation:

$$BV'' - \frac{(BA)'}{A} V' + \frac{i}{c} \frac{BA^2}{R_2} V = -\frac{i}{c} ABF(\theta) \quad (9)$$

In the case of a toroidal shell of elliptical cross-section (Figure 1) we have:

$$\left. \begin{aligned} x &= B \cos \varphi, \quad y = B \sin \varphi, \quad z = b \cos \theta \\ A &= aa = a(1 - e \sin^2 \theta)^{1/2} \\ B &= R_0 = R(1 + \lambda \sin \theta) \\ R_1 &= \frac{a^2}{b} (1 - e \sin^2 \theta)^{3/2} \\ R_2 &= \frac{a^2}{b \lambda \sin \theta} (1 - e \sin^2 \theta)^{1/2} (1 + \lambda \sin \theta) \end{aligned} \right\} \quad (10)$$

Equation (9) now becomes:

$$\begin{aligned} \varrho V'' - \cos \theta \left(\lambda - \frac{e\varrho}{\alpha^2} \sin \theta \right) V' + i2k^2 \alpha \sin \theta V = i2k^2 \alpha \frac{a}{b} R^2 \varrho^2 \left\{ \alpha(1+\nu)q_0 + \right. \\ \left. + \frac{a}{b} \left[\frac{\alpha\varrho}{\lambda \sin \theta} q_n + \frac{\alpha}{\varrho \sin \theta} \left(1 - \frac{\varrho}{\lambda \alpha^2 \sin \theta} \right) \frac{\Omega}{aR} \right]' \right\} \end{aligned} \quad (11)$$

To remove the indeterminate form of the right-hand side of this equation at $\theta = 0, \pi$, let us introduce a new function:

$$X = \frac{b}{R^2} V - i2k^2 \frac{\varrho}{b} \Omega \operatorname{ctg} \theta \quad (12)$$

Equation (11) reads then:

$$\begin{aligned} (1 + \lambda \sin \theta) X'' - \cos \theta \left[\lambda - \frac{e(1 + \lambda \sin \theta)}{1 - e \sin^2 \theta} \sin \theta \right] X' + \\ + i2k^2 \sqrt{1 - e \sin^2 \theta} \sin \theta \cdot X = i2k^2 \sqrt{1 - e \sin^2 \theta} [f_1(\theta) \sin \theta + f_2(\theta)] \end{aligned} \quad (13)$$

where

$$\begin{aligned} f_1(\theta) = aq'_H (3 + 3\lambda \sin \theta + \lambda^2 \sin^2 \theta) + a\lambda q_H (2 + \nu) (2 + \lambda \sin \theta) \cos \theta - \\ - \nu b q_V (1 + \lambda \sin \theta)^2 - \frac{i2k^2}{b} \lambda \Omega \cos \theta \\ f_2(\theta) = q'_H R + q_H (2 + \nu) a \cos \theta - i \frac{2k^2}{b} \Omega \cos \theta \end{aligned} \quad (14)$$

The radial and axial components of the load intensity q_H, q_V are related to the previous components q_n, q_0 by the equations:

$$\left. \begin{aligned} q_V &= \frac{1}{a} (1 - e \sin^2 \theta)^{-1/2} (a q_n \cos \theta - b q_0 \sin \theta) \\ q_H &= \frac{1}{a} (1 - e \sin^2 \theta)^{-1/2} (b q_n \sin \theta + a q_0 \cos \theta) \end{aligned} \right\} \quad (15)$$

and the load function Ω defined by (5) now equals

$$\Omega = aR \int_0^\theta (1 + \lambda \sin \theta) (1 - e \sin^2 \theta)^{1/2} q_V d\theta + C_Q \quad (16)$$

All the desired values may be determined in terms of the complex function X by the following relations:

$$\begin{aligned}
 T_\theta &= \lambda(1 - e^{\pi} \sin^2 \theta)^{-1/2} (1 + \lambda \sin \theta)^{-2} \left[-\frac{1}{2k^2} X_i \cos \theta + \right. \\
 &\quad \left. + \frac{b}{a^2} (1 + \lambda \sin \theta) \Omega \sin \theta \right] \\
 T_\varphi &= -\frac{1}{2k^2} (1 - e \sin^2 \theta)^{-1/2} \frac{d}{d\theta} \left[X_i (1 + \lambda \sin \theta)^{-1} \right] + R(1 + \lambda \sin \theta) q_H \\
 N_\theta &= -\frac{1}{2k^2} (1 - e \sin^2 \theta)^{-1/2} (1 + \lambda \sin \theta)^{-2} \left[\frac{b}{a} X_i \sin \theta + \right. \\
 &\quad \left. + \frac{1}{R} (1 + \lambda \sin \theta) \Omega \cos \theta \right] \\
 M_\theta &= -\frac{c}{2k^2} (1 - e \sin^2 \theta)^{-1/2} (1 + \lambda \sin \theta)^{-2} \left[(1 + \lambda \sin \theta) \frac{dX_r}{d\theta} + \right. \\
 &\quad \left. + (1 + \nu) \lambda X_r \cos \theta \right] \\
 M_\varphi &= -\frac{c}{2k^2} (1 - e \sin^2 \theta)^{-1/2} (1 + \lambda \sin \theta)^{-2} \left[\nu(1 + \lambda \sin \theta) \frac{dX_r}{d\theta} + \right. \\
 &\quad \left. + (1 + \nu) \lambda X_r \cos \theta \right]
 \end{aligned} \tag{17}$$

$$\left. \begin{aligned}
 \vartheta &= -\frac{R}{bE\delta} (1 + \lambda \sin \theta)^{-1} X_r \\
 u_V &= -\int_{\theta_1}^{\theta} \left[a\vartheta \cos \theta + \frac{b}{E\delta} (T_\theta - \nu T_\varphi) \sin \theta \right] d\theta + C_V \\
 u_H &= \frac{R}{E\delta} (1 + \lambda \sin \theta) (T_\varphi - \nu T_\theta)
 \end{aligned} \right\} \tag{18}$$

C_V = constant of integration

Thus the problem is reduced to evaluation of the complex function X satisfying Eq. (13) and suitable boundary conditions.

4. ASYMPTOTIC INTEGRATION OF EQ. (13)

Setting the right-hand side of Eq. (13) equal to zero, we obtain the corresponding homogeneous differential equation:

$$(1 + \lambda \sin \theta) X_0'' - \cos \theta \left[\lambda - \frac{e(1 + \lambda \sin \theta)}{1 - e \sin^2 \theta} \sin \theta \right] X_0' + \\ + i2k^2 \sqrt{1 - e \sin^2 \theta} \sin \theta X_0 = 0 \quad (19)$$

Let us restrict our attention temporarily to the interval

$$0 \leq \theta \leq \frac{\pi}{2} \quad (20)$$

and define new functions x and W by the relations:

$$dx = \sqrt{2i} k \sqrt[4]{1 - e \sin^2 \theta} \cdot \sqrt{\frac{\sin \theta}{1 + \lambda \sin \theta}} d\theta, \quad x = \sqrt{2i} \xi \quad (21)$$

$$\xi = k \int_0^\theta \sqrt[4]{1 - e \sin^2 \theta} \sqrt{\frac{\sin \theta}{1 + \lambda \sin \theta}} d\theta \quad (22)$$

$$W = X_0 (i2k^2)^{1/4} (1 + \lambda \sin \theta)^{-3/4} (1 - e \sin^2 \theta)^{-1/8} (\sin \theta)^{1/4} \quad (23)$$

Eq. (19) now becomes

$$\frac{d^2 W}{dx^2} + (1 + \Delta) W = 0 \quad (24)$$

where

$$\Delta = \frac{1}{i2k^2} \frac{5}{16} \frac{1}{\sin^3 \theta (1 - e \sin^2 \theta)^{3/2}} \left\{ 1 + 0.6 \lambda \sin \theta - 0.2 \sin^2 \theta - \right. \\ \left. - 2.2 \lambda \sin^3 \theta - 3 \frac{\lambda^2 \cos^2 \theta \sin^2 \theta}{1 + \lambda \sin \theta} + e \sin^2 \theta \left[-2.2 \frac{1 + \lambda \sin \theta}{1 - e \sin^2 \theta} + \right. \right. \\ \left. \left. + 3 \frac{\lambda^2 \cos^2 \theta \sin^2 \theta}{1 + \lambda \sin \theta} + 2.4 \lambda \sin \theta \right] \right\} \quad (25)$$

Since Δ is small in comparison with unity unless the angle θ is near the singular line $\theta = 0$, we may take in Eq. (24):

$$\Delta \cong \frac{1}{i2k^2} \frac{5}{16\theta^3} \quad (26)$$

Furthermore, integrating the right-hand side of (22) by expanding the integrand in power series with respect to θ , we find

$$x = \sqrt{2i} k \frac{2}{3} \theta^{3/2} [1 + g(\theta, \lambda, e)] \approx k \sqrt{2i} \frac{2}{3} \theta^{3/2} \text{ near } \theta = 0 \quad (27)$$

since the function $g(\theta, \lambda, e)$ vanishes at $\theta = 0$,

$$g(\theta, \lambda, e) = 0 \quad (28)$$

Combining the approximate equalities (26) and (27) we may express the additional term Δ in Eq. (23) by the variable x , obtaining:

$$\frac{d^2 W}{dx^2} + \left(1 + \frac{5}{36x^2}\right) W = 0 \quad (29)$$

The same Bessel equation has been obtained by E. F. Zenova and V. V. Novoshilov⁵ while investigating the symmetrical deformation of a toroidal shell with circular section. Since the solution of this equation is discussed in their paper, we will only consider the final relations.

Returning to the basic function X_0 we have

$$X_0 = (1 + \lambda \sin \theta)^{3/4} (1 - e \sin^2 \theta)^{1/8} [(C_1 + iC_2) X_1 + (C_3 + iC_4) X_2] \quad (30)$$

where C_n are constants of integration and the complex functions X_1 , X_2 , and their first derivatives are tabulated versus ξ , defined by (22), in reference 1.

$$\text{For negative angles } \theta, \quad -\frac{\pi}{2} \leq \theta \leq 0 \quad (31)$$

we must replace the variable ξ by ζ :

$$\zeta = k \int_0^\psi \sqrt[4]{1 - e \sin^2 \psi} \sqrt{\frac{\sin \psi}{1 - \lambda \sin \psi}} d\psi \quad (32)$$

where

$$\psi = -\theta \quad (33)$$

and the desired function X_0 may now be represented in the form

$$X_0 = (1 + \lambda \sin \theta)^{3/4} (1 - e \sin^2 \theta)^{1/8} [(C_1 + iC_2) X_3 + (C_3 + iC_4) X_4] \quad (34)$$

where functions X_3 , X_4 and their first derivatives are tabulated versus ζ in reference 1.

The particular solution of the non-homogeneous equation (13) may be found by applying the known method of variation of the constants C_n , or by using the asymptotic method as shown by R. A. Clark² and by R. A. Clark and E. Reissner³.

In the latter case the particular integral may be represented in the form

$$X_p = f_1(\theta) + i(2k^2)^{1/3} (1 - e \sin^2 \theta)^{1/2} f_2(\theta) Z(\eta) \quad (35)$$

where

$$\eta = -(2k^2)^{1/3} (1 - e \sin^2 \theta)^{1/2} \sin \theta \quad (36)$$

and the complex function $Z(\eta)$ is a solution of the Bessel equation

$$\frac{d^2 Z}{d\eta^2} - i\eta Z = 0 \quad (37)$$

asymptotic to i/η for large η :

$$\lim_{\eta \rightarrow \infty} (\eta Z) = i \quad (38)$$

This complex function and its derivative are tabulated in reference 2.

For large θ , in view of (36) and (38), we have

$$Z(\eta) = -i \frac{1}{(2k^2)^{1/3} (1 - e \sin^2 \theta)^{1/2} \sin \theta} \quad (39)$$

and then, in accordance with (35)

$$X_p = f_1(\theta) + \frac{f_2(\theta)}{\sin \theta}, \quad \text{for } \theta \gg 0 \quad (40)$$

This solution may be obtained immediately by observing that for large θ , all the terms except the last one on the left hand of Eq. (13) may be neglected, since we assume that $2k^2 \gg 1$.

Thus, using asymptotic methods for finding both the general and particular integrals of the basic Eq. (13), we obtain:

$$\left. \begin{aligned} X &= X_0 + X_p = (1 + \lambda \sin \theta)^{3/4} (1 - e \sin^2 \theta)^{1/8} [(C_1 + iC_2) X_l + \\ &+ (C_3 + iC_4) X_n] + f_1(\theta) + i(2k^2)^{1/3} (1 - e \sin^2 \theta)^{1/2} f_2(\theta) Z(\eta); \\ l &= 1, n = 2, \text{ or } l = 3, n = 4 \text{ according to (20) and (31) respectively.} \end{aligned} \right\} \quad (41)$$

All the unknown functions X_l , X_n , Z and their first derivatives are tabulated.

When $e = 0$ this formula reduces, as it should, to the corresponding formulas for the circular torus developed by the author in reference 4.

A particular case of the problem considered, the bending of curved elliptical tubes, has recently been investigated by R. A. Clark and E. Reissner in reference 3.

5. CONCLUSION

The expression of the function X defined by (41) in a closed form by means of simple asymptotic formulas makes possible the qualitative analysis* of the relations (17) and (18).

* Such an analysis was carried out by the author for a circular torus in reference 4.

This analysis shows that the toroidal shell behaves in principle like any shell of revolution (meaning that far enough from the edge parallels, the state of stress is practically a membrane one), excluding the regions adjacent to the singular parallels $\theta = 0, \pi$.

REMARKS

Since this paper was completed, two new works dealing with toroidal shells have been brought to the author's attention. R. A. Clark⁶ refined his asymptotic method of integration developed in his previous work², and G. D. Galletly⁷ proved that one must be very cautious in applying Geckeler's method to the calculation of toroidal shells even for regions far enough from the singular parallels.

ACKNOWLEDGMENT

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REAGENT FOR RAPID MICROSCOPIC CARBIDE DETECTION IN AUSTENITIC STAINLESS STEELS

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ABSTRACT

A gold-base acidic reagent reveals carbides in ferrous alloys by means of selective plating of the different phases. The surface is coated with a gold film which is subsequently dislodged by the pressure of hydrogen over the more reactive phase while retained over the less reactive carbides.

The quality and corrosion resistance of a stainless steel of the high chrome-nickel type are mainly governed by the free carbide content of its microstructure. These steels, however, do not lend themselves to reliable microscopic examination; even small amounts of cold work preclude effective etching, and owing to the tendency of carbides to precipitate along grain boundaries, distinction is not always possible even with an effective etch. Microscopic analysis is thus necessarily confined to identifying carbides of sizes exceeding the width of the grain boundary. (These are discernible as white globules). As a result, it has so far proved impossible to determine the cause of deterioration in austenitic steels containing carbides in a very finely dispersed condition, and the whole matter often has to rest on guesswork.

Experiments with the gold-base reagent developed recently by one of the authors¹ have demonstrated its suitability for differentiating carbide precipitates from other ambiguous phases in all types of steels, by means of selective plating. Its main value lies in the rapid detection of carbides in austenitic steels, irrespective of cold work.

Figures 1 and 2 show photomicrographs of 18/8 stainless steel etched with this reagent. Carbides precipitated at the austenitic grain boundaries are clearly revealed, while the boundaries themselves are indistinguishable.

Experimental Procedure

A metallographically prepared steel specimen is immersed for 20 seconds in a reagent of the following nominal composition:

AuCl ₃ (anhydrous)	0.223 g
HCl (30%)	10 cc
H ₂ O	40 cc

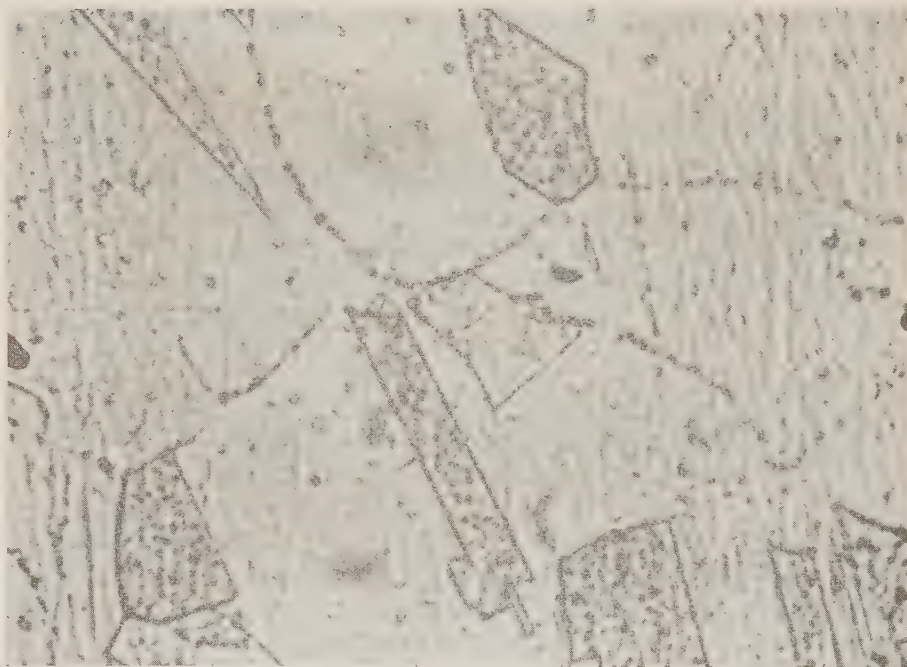


Figure 1

Cold worked to 35% deformation

Austenitic stainless steels of the 18/8 type. Etch—Taub's reagent. Magnification $\times 1500$.

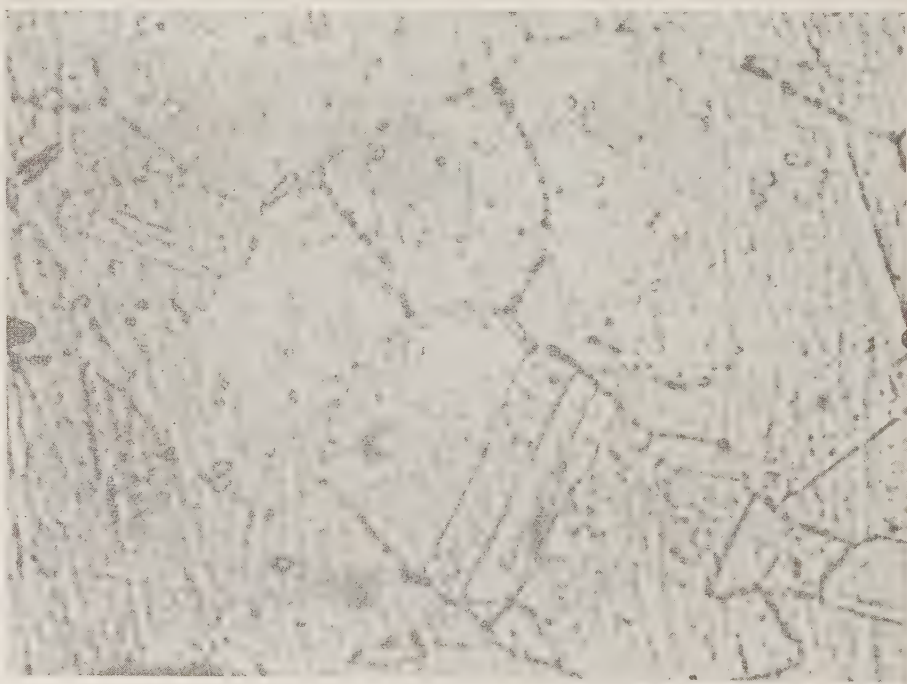


Figure 2

Annealed

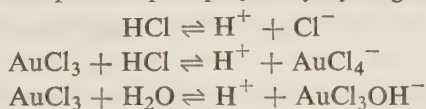
Carbides are plated, while grain boundaries remain unetched and are indicated by stringers only. Continuous dark twin boundaries indicate submicroscopic carbide precipitation.

Next, the gold-plated specimen is washed under the tap and at the same time lightly rubbed with cotton wool in order to dislodge the loose part of the gold film over the non-carbide areas, leaving the firmly adhering plate over the carbides. Finally, the specimen is washed in alcohol and dried in a stream of hot air.

Mechanism of the etching reaction

The contribution of the hydrochloric acid was studied in tests using the nominal gold chloride content (0.223 g AuCl_3 per 50 cc solution) combined with varying acid-water ratios. In Figure 3, curve I gives the immersion time required for detaching 10% of the gold plate over the ferritic areas and curve II the minimum time required for complete loosening, both plotted against acid concentration. The contribution of the gold chloride was studied in similar tests, this time using the nominal acid-water ratio (1:4); results are shown in Figure 4, with curves I and II as above plotted against gold chloride concentration.

The tests showed that the qualitative effect of varying the concentration of either the hydrochloric acid or gold chloride is the same. This is to be expected, considering the following equilibria and the important part played by hydrogen (see below):



The reaction taking place upon immersion in the gold reagent of a steel specimen containing free carbides in a ferritic or austenitic matrix can be described as follows:

1. Gold is precipitated from the solution and deposited onto both phases.
2. At the same time, hydrogen is formed at the surface.

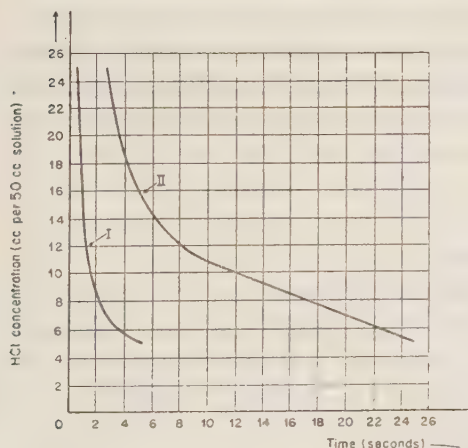


Figure 3

Immersion time required to detach 10% (curve I) and all (curve II) of gold plate over ferritic areas plotted against acid concentration

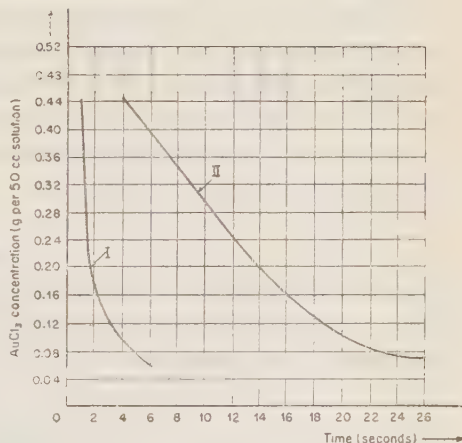


Figure 4

Same as Figure 3, but plotted against gold chloride concentration

The hydrogen ions can reach the steel surface, where they are discharged either through the gold plate (by diffusion) or directly through discontinuities in the plate over non-metallic inclusions.* The accumulating gas builds up pressure at a rate proportional to that of the reaction, i.e. to the concentration of the hydrogen ions in the solution. This pressure gradually loosens and finally breaks the bond between steel and plate; and, as it is mainly concentrated over the ferritic or austenitic areas of the specimen (owing to the substantially lower degree of attack of hydrochloric acid on carbides), the plate is selectively removed over the former while retained over the latter.

This hypothesis was verified by treating specimens with a reagent of much higher hydrogen ion concentration (AuCl_3 — 0.223 g; HCl (30%) — 50 cc), with immersion times ranging from one to two minutes. Subsequent microscopic examination showed the plate removed over the carbide areas as well. In tests under standard conditions (nominal reagent, 20 sec immersion), however, no unplated carbide or residual plate over ferrite were observed. Figures 3 and 4 show that a minimum immersion time of 12 to 13 sec is required for complete removal of the plate over the ferrites. The time required for its complete removal over the carbide was not actually determined for the nominal reagent, but repeated immersions totalling 200 sec failed to produce appreciable loosening.

It is also of interest to note that examination of pearlite steels treated with the nominal reagent showed pearlite colonies of interlamellar spacing of less than $(6.7 \pm 0.3) \times 10^{-4}$ mm continuously plated, while carbide lamellae in pearlite, with wider spacing, were clearly revealed.

CONCLUSION

The gold reagent permits rapid positive identification of certain ambiguous phases in steel microstructure, by means of its selective action on iron carbides in ferrous alloys. Earlier methods for identifying cementite in steels are rather tedious, owing to the lengthy process and boiling-point temperatures required for etching with alkaline sodium picrate and ferricyanide solutions, and can be advantageously replaced by the simplified new procedure.

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* The latter alternative is supported by the easier detachability of the plate near such inclusions.

VISCOUS STRAIN HARDENING IN BREAD DOUGHS

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In connection with an investigation into the rheological properties of dough, we have carried out a series of experiments with dough cylinders of two different types of flour, namely *Triticum vulgare* and *Triticum durum*. These have shown that response to load consists in both cases of the following three types of deformation: instantaneous strain, delayed strain and viscous flow. Some evidence suggested that a plastic flow with a finite yield point was coupled in parallel to each of these deformations. All parameters were stress and strain dependent. The differences between the two types of dough were quantitative, and it could generally be said that *durum* dough of the same water content as *vulgare* was much more rigid and viscous. Even when water was added to the *durum* dough in order to achieve low rigidity equal to that of the *vulgare* dough (in accordance with Halton's¹ extrusion criterion), its viscosity remained higher.

One feature in which the two doughs differed spectacularly was the property of viscous strain hardening. As already mentioned, all behaviour was non-linear. This was especially pronounced with *vulgare* in elastic deformation and with *durum* in viscous flow. Thus there was considerable stress softening and strain hardening of rigidity in *vulgare*, and similar effects with regard to viscosity in *durum*. As the major part of deformation of dough stems from viscous flow, the pronounced effect of viscous strain hardening of *durum* dough is of great importance. When *durum* specimens were stretched in the extensimeter on a mercury bath up to an axial stress of 9000 dynes/cm², no sign of necking was observed, whereas *vulgare* specimens similarly stretched already developed necking at a stress of 6000 dynes/cm². This provided visual confirmation of the already observed behaviour of viscous strain hardening in *durum*: when necking starts at the weakest section of the cylinder, with resulting excessive deformation, the material at that point hardens, i.e. the viscosity increases, and the tendency to necking is transferred to the next weakest section, where the same course of events is repeated. Thus the cylindrical shape is maintained. The elastic strain hardening of *vulgare* is of lesser importance, as the elastic deformation is small compared with the viscous deformation, and thus necking is very little counteracted in *vulgare*. Nevertheless *vulgare* is called a "strong" flour, having good baking qualities, while *durum*, on the other hand, is considered a "weak"

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flour. These facts may seem to contradict the observations reported above with regard to necking. In actual fact the two are reconcilable. The fact that *vulgaris* has a low viscous strain hardening is responsible for the preservation of a short time of relaxation as the material expands in the oven, while the high viscous strain hardening of *durum* results in an increasing time of relaxation, which in turn causes a brittle fracture as the material expands, a property known to the bakers as "shortness". When it is remembered in addition that *durum* is generally stiffer than *vulgaris*, it will be understood why, for equal deformations (e.g. for equally developed loaves of bread), the former will rupture before the latter, thus permitting the escape of hot gases which in turn will not allow the development of a sound loaf. The necking of a dough specimen in a tensile test is thus an indication of its suitability for bread-making, for it shows that the material has no viscous strain hardening and is thus quite ductile.

A complete report on the research of which the above forms a part will be published elsewhere. The research was planned as a continuation of the fundamental investigations on flour-dough carried out a quarter of a century ago by Schofield and Scott-Blair, concerning which pp. 91-95 of Scott-Blair and Reiner² should be consulted.

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SECOND-ORDER TERMS OF DEFORMATION IN SIMPLE SHEAR

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ABSTRACT

Through the choice of various measures of deformation and by means of a graphical method based on Mohr's circle, simple shear yields second-order terms even in infinitesimal deformation, which cannot, as is done in the classical theory, be neglected. These terms vary with the choice of the measure of deformation, but are all positive in the direction of the shear and negative in the direction normal to it. Five measures of deformation are discussed, all degenerating to the classical Cauchy measure in pure infinitesimal deformation, i.e. when no rotation of the principal axes of deformation takes place from the initial to the final state.

1. Simple and pure shear

Simple shear is a distortion (change of shape), as shown in Figure 1. The measure of its deformation is a function of the displacement gradient Γ .

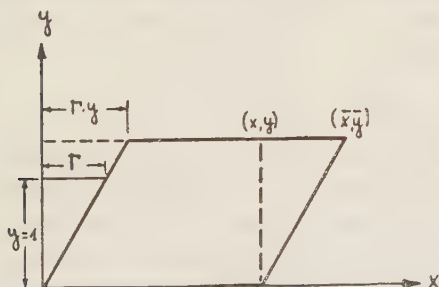


Figure 1
Simple shear

Γ displacement gradient

x, y initial coordinates

\bar{x}, \bar{y} displaced (final) coordinates

Simple shear can be considered to consist of a *pure shear* and a *rigid rotation* of the body with respect to an axis perpendicular to the plane of deformation (in this case the z -axis). In pure shear both the cross-sectional area and the volume of an element remain unchanged, and only a distortion takes place.

Love² gives the following geometrical relations for pure shear:

* This paper forms part of the thesis submitted by the author in 1953 to the Technion - Israel Institute of Technology in compliance with the requirements for the degree of Master of Science.

Let e_1 denote the relative change in length of lines parallel to the x -axis, and e_2 of those parallel to the y -axis. Due to the shear, each point, the initial coordinates of which are (x, y) , will move to the new coordinates $(x + e_1x, y + e_2y)$. The change in area of the plane element will be in the ratio

$$(1 + e_1)(1 + e_2): 1. \quad (1.1)$$

The condition for pure shear, namely, that there should be no change in area, demands that this ratio be equal to 1. Therefore, either e_1 or e_2 denotes a contraction, while the other of the pair denotes an extension. If we assume the x -direction to be that of the contraction, and we put

$$e_2 - e_1 = 2 \tan \alpha \quad (1.2)$$

where α is measured from y to x , then from (1.1) and (1.2) we readily find

$$1 + e_1 = \sec \alpha - \tan \alpha = l_i; \quad 1 + e_2 = \sec \alpha + \tan \alpha = l_j. \quad (1.3)$$

It can be shown (for a full proof see Love², Art. 3) that if new axes x, y are chosen, resulting from a rotation by $\pi/4 - \alpha/2$ in the sense from x to y , then each point whose initial coordinates were x, y will move, due to shear, to the new coordinates \bar{x}, \bar{y} such that

$$\bar{x} = x + 2y \tan \alpha; \quad \bar{y} = y. \quad (1.4)$$

All points (x, y) thus undergo a displacement parallel to the x -axis which in accordance with (1.4) is proportional to their distance from the x -axis. This is the case of simple shear, where α is the *angle of shear*, and $2 \tan \alpha$ is the *amount of shear* or the *shear gradient*. Hence from (1.4), comparing Figure 1,

$$I' = 2 \tan \alpha \quad (1.5)$$

The above relations as given by Love, which yield the directions of the principal axes, permit a graphical construction (see Figure 2). If we follow the distortion of a circle, the radius of which in the unstrained state is unity, it will transform, due to shear, into an ellipse possessing the *same area* as that of the circle. The principal axis of the ellipse i (compare Figure 3) will be inclined to the x -axis by the angle

$$\beta = \frac{\pi}{4} - \frac{\alpha}{2}. \quad (1.6)$$

In the unstrained state this axis will have the direction \bar{i} . The angle between i and \bar{i} is α . The directions \bar{i} and \bar{j} can also be looked upon as the principal axes of the reciprocal strain ellipse. The lengths of the principal axes are l_i and l_j given by Eq. (1.3).

Three states of simple shear for various values of the gradient I' are shown in Figure 2. Their magnitudes are considerable, and they therefore constitute finite deformations.

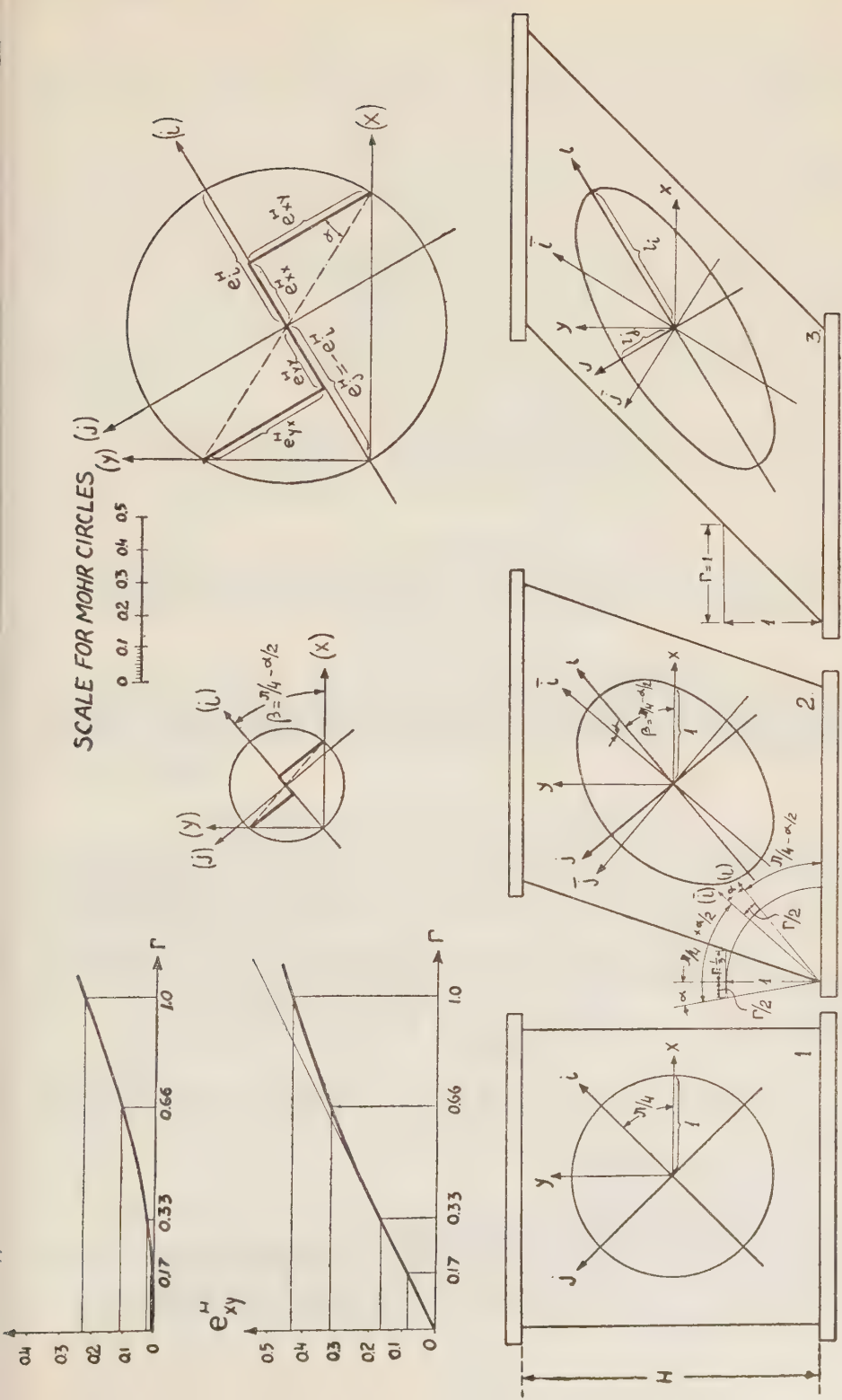


Figure 2

Mohr circles and strain-gradient diagrams for simple shear in the Hencky measure

e strain tensor; Γ displacement gradient; α angle of rotation; \bar{i}, \bar{j} principal directions before deformation; i, j principal directions after deformation; (i) parallel to \bar{i}

The deformation of a continuous material is uniquely determined by the extensions (or contractions) of line elements lying in the principal directions. Consequently if the principal strains e_i, e_j are defined, all other components of strain in any other direction can then be found analytically, or graphically by means of Mohr's circle. This implies that if in the final state there is no change in length of line elements in the principal direction, i.e. $l_i = l_0$, then *the body is not deformed*. However, if a line element not lying in a principal direction does not undergo any change in length, this does not necessarily imply that there is no component of deformation in this direction. For instance, from Figure 2 we conclude that the radius of the initial circle in the x -direction remains unchanged in length in all subsequent states of simple shear, and in spite of this a deformation component e_{xx} might exist, as will be shown below.

The concept of deformation cannot be established unambiguously. While deformation is related to certain unambiguous physical concepts, the form of this relation is arbitrary. Any form of Eq. (2.1) fulfilling the conditions listed above will be satisfactory.

In the classical Theory of Elasticity the measure of deformation used is the one introduced by Cauchy, defined for the principal direction by

$$e_i^C = \frac{l_i - l_0}{l_0} = \frac{\Delta l}{l_0}, \quad (2.2)$$

but other measures have been proposed for finite deformation. In the following, various measures of deformation are considered, and consequences connected with them investigated.

3. Various measures of deformation

Discussions on finite deformations are included in the fundamental publications of the classical theory of elasticity, such as by Green, St. Venant, Kirchhoff, Cauchy, Kelvin and Tait and others*.

Five measures of deformation have been postulated so far. They are:

- (i) *The Cauchy measure* in accordance with Eq. (2.2).

Here the difference in length in the principal directions is related to the initial length.

- (ii) *The Swainger measure*

$$e_i^S = \frac{l_i - l_0}{l_i} = \frac{\Delta l}{l_i}. \quad (3.1)$$

Here the ratio is taken with respect to the final length. There is a certain relation between Cauchy's and Swainger's measures which will be stated below.

* For references see Truesdell⁵ (1952).

(iii) *The Hencky measure*

According to his definition the increment of deformation at every stage between the initial and final states is $de = \frac{dl}{l}$, and hence

$$e_i^H = \int_{l_0}^{l_i} de = \int_{l_0}^{l_i} \left(\frac{dl}{l} \right) = \ln \frac{l_i}{l_0}. \quad (3.2)$$

This is also known as the logarithmic or natural strain.

(iv) *The Green-St. Venant measure*

This is also known as the Lagrangean measure. In its conception it resembles Lagrange's approach in hydrodynamics where the initial coordinates of the material points are regarded as the independent variables.

Green's measure is

$$e_i^G = \frac{1}{2} \left[\left(\frac{l_i}{l_0} \right)^2 - 1 \right]. \quad (3.3)$$

(v) *The Almansi-Hamel measure*

This measure is related to the final position of the body, and is therefore also known as the Eulerian measure. For the principal component of strain we get

$$e_i^A = \frac{1}{2} \left[1 - \frac{1}{(l_i/l_0)^2} \right]. \quad (3.4)$$

Between Green's and Almansi's measures there exists the same relation as between Cauchy's and Swainger's, to be shown and proved later.

In addition to the five main measures, other definitions for measures of deformation have been suggested*.

4. *The components of deformation*

When a measure of deformation is chosen, the principal components of its tensor result immediately. Then any other components of the tensor e_{rs} in any other directions, e.g. x and y , can be found analytically or graphically by means of Mohr's circle.

The analytical method is based on the equation of the strain ellipsoid

$$e_{\alpha\beta} x_{\alpha} x_{\beta} = c \quad (4.1)$$

where repeated indices imply summation.

* For complete references see Truesdell⁵, pp. 141-145.

The matrix of e_{rs} , in the three-dimensional case, is

$$||e_{rs}||_{x,y,z} = \begin{vmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{vmatrix} \quad (4.2)$$

and with respect to the principal axes

$$||e_{rs}||_{i,j,k} = \begin{vmatrix} e_i & 0 & 0 \\ 0 & e_j & 0 \\ 0 & 0 & e_k \end{vmatrix} \quad (4.3)$$

The transformation of the strain ellipsoid from any axes to its canonic form in the principal axes yields the following known relations between the components in the two-dimensional case*:

$$e_i = \frac{e_{xx} + e_{yy}}{2} \pm \sqrt{\left[\frac{e_{xx} - e_{yy}}{2}\right]^2 + e_{xy}^2} \quad (4.4)$$

One solution of (4.4) is e_i , the other e_j . The principal directions are found from the relation

$$\tan 2\beta = \frac{2e_{xy}}{e_{xx} - e_{yy}} \quad (4.5)$$

Equations (4.4) and (4.5) are valid for any symmetrical tensor of rank two, $t_{rs}(r,s=1,2)$, expressed in rectangular coordinates. They are the basis for which Mohr's circle is a graphical representation.

Consequently the various components can also be found by a grapho-analytical method based on Mohr's circle.

Mohr's circle is determined by the directions of principal axes, and the values of the principal components.

The centre distance and the radius of the circle are given by

$$\begin{aligned} \overline{OC} &= \frac{e_i + e_j}{2} \\ R &= \frac{e_i - e_j}{2} \end{aligned} \quad (e_i > e_j) \quad (4.6)$$

From the right angle AFD , Figure 4, considering that the i -direction is inclined to the x -direction by an angle $\beta = \frac{\pi}{4} - \frac{\alpha}{2}$ [see (1.6)], we find that $\angle CAF = \alpha$.

The component e_{xx} is given by \overline{OF} and e_{yy} by \overline{OG} ; e_{xy} equals \overline{AF} . Hence we have for the components in the x,y directions the following values:

* For the derivation of these formulac see, for example, Ollendorff³, Section IV.5.

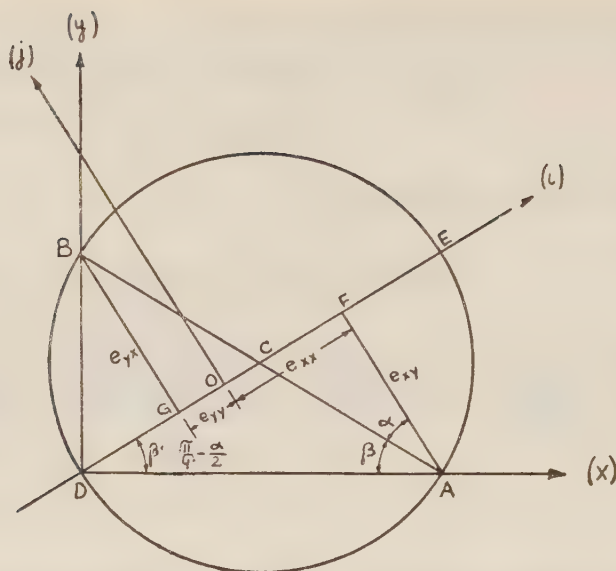


Figure 4

Mohr's circle for plane deformation

(i), (j) parallels to the principal directions after deformation
 e_{xy} , e_{xx} , e_{yy} components of strain in x, y -directions

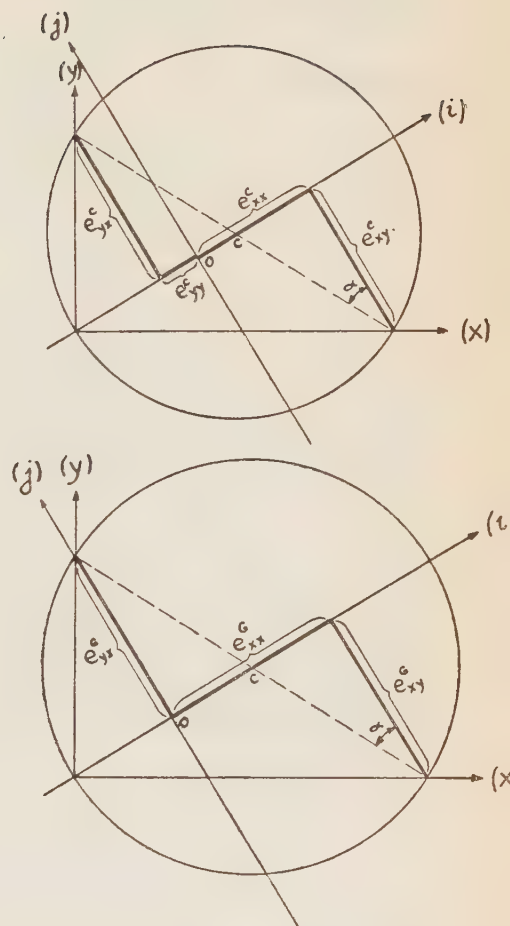
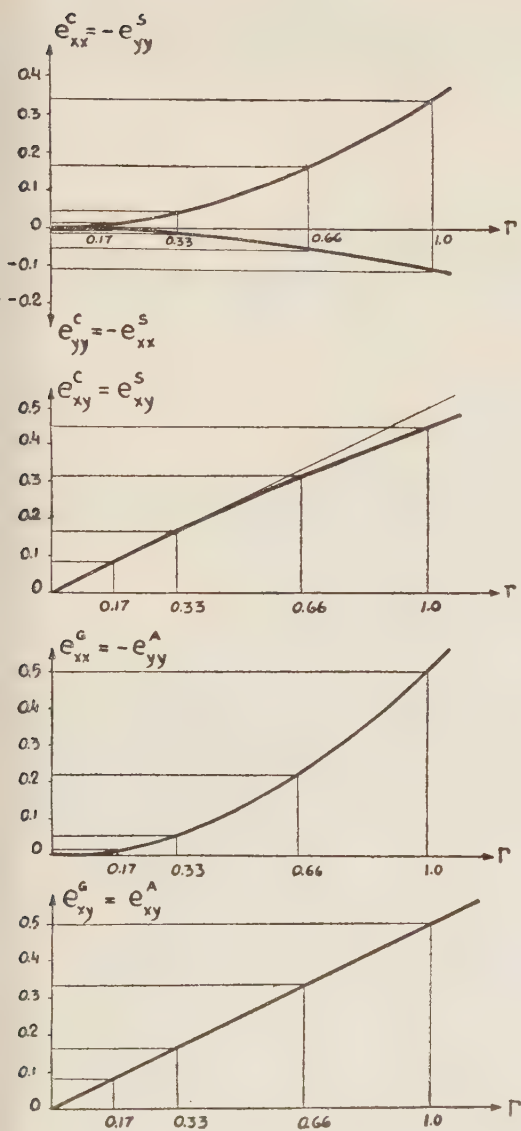
$$\begin{aligned}
 e_{xy} = e_{yx} &= R \cos \alpha = \frac{e_i - e_j}{2} \cos \alpha \\
 e_{xx} &= \overline{OC} + R \sin \alpha = \frac{e_i + e_j}{2} + \frac{e_i - e_j}{2} \sin \alpha \\
 e_{yy} &= \overline{OC} - R \sin \alpha = \frac{e_i + e_j}{2} - \frac{e_i - e_j}{2} \sin \alpha
 \end{aligned} \tag{4.7}$$

This is therefore a general method for finding any desired component of plane deformation, once a measure of deformation is chosen and defined for the principal directions, i.e. when e_i, e_j are known. Only for Green's and Almansi's measures are tensor expressions for e_{rs} known*. For the other measures, when no such expressions exist, the above method makes it possible to determine all components of e_{rs} .

5. Components of deformation in various measures

The numerical values for the components in the principal directions and x, y -directions are listed below for various states of simple shear, namely $I = 0; \frac{1}{2}; 1$. The corresponding Mohr's circles and the e_{xx}, e_{yy}, e_{xy} diagrams as functions of I are given in Figure 2 and Figure 5.

* Hanin and Reiner¹ have reduced the Hencky measure to the Almansi measure.



SCALE FOR MOHR CIRCLES



Figure 5

Mohr circles and strain-gradient diagrams in the Cauchy-Swainger and the Green-Almansi measures
Mohr circles for $\Gamma = 1$

(i) *Hencky's measure* — e^H .

For this measure $e_i^H = -e_j^H$. The proof is as follows: The area of the unit circle equals $\pi \times 1^2$. The area of the ellipse is $\pi l_i \cdot l_j$. In simple shear the area remains unchanged and consequently

$$l_i l_j = 1. \quad (5.1)$$

We assume $l_0 = 1$, and get, using (5.1),

$$e_i^H = \ln \frac{l_i}{l_0} = \ln l_i = \ln \frac{l_i}{l_i l_j} = \ln \frac{1}{l_j} = -\ln l_j = -e_j^H$$

From equations (4.6), (4.7), and substituting $e_i^H = -e_j^H$, we obtain

$$\begin{aligned} R^H &= e_i^H; \overline{OC} = 0 \\ e_{xy}^H &= e_i^H \cos \alpha = \ln l_i \cdot \cos \alpha \\ e_{xx}^H &= -e_{yy}^H = e_i^H \sin \alpha = \ln l_i \cdot \sin \alpha. \end{aligned} \quad (5.2)$$

From (1.5), values for $\sin \alpha$ and $\cos \alpha$ are found, and l_i and l_j can then be expressed through I from (1.3). Finally we find

$$\begin{aligned} e_{xy}^H &= \frac{1}{\sqrt{1 + I^2/4}} \ln [\sqrt{1 + I^2/4} + I/2] \\ e_{xx}^H &= \frac{1}{\sqrt{1 + 4/I^2}} \ln [\sqrt{1 + I^2/4} + I/2] = -e_{yy}^H \end{aligned}$$

l_i, l_j can also be measured from Figure 2 to scale. The components e_{xx}, e_{yy}, e_{xy} can also be measured from Mohr's circles.

(ii) *Cauchy's measure* — e^C .

From (2.2) and (1.3)

$$\begin{aligned} e_i^C &= l_i - 1 = \sec \alpha + \tan \alpha - 1 \\ e_j^C &= l_j - 1 = \sec \alpha - \tan \alpha - 1 \end{aligned}$$

Using (4.6):

$$\begin{aligned} R^C &= \frac{1}{2}(e_i^C - e_j^C) = \tan \alpha \\ \overline{OC}^C &= \frac{1}{2}(e_i^C + e_j^C) = \sec \alpha - 1. \end{aligned}$$

Substitution into (4.7) yields

$$\begin{aligned} e_{xy}^C &= \sin \alpha \\ e_{xx}^C &= \frac{1 + \sin^2 \alpha}{\cos \alpha} - 1 \\ e_{yy}^C &= \cos \alpha - 1. \end{aligned} \quad (5.3)$$

The corresponding diagrams are shown in Figure 5.

(iii) *Swainger's measure* — e^S .

Following the definition of this measure in (3.1) we have

$$e_i^S = 1 - \frac{1}{l_i} = 1 - \frac{\cos \alpha}{1 + \sin \alpha}$$

$$e_j^S = 1 - \frac{1}{l_j} = 1 - \frac{\cos \alpha}{1 - \sin \alpha}.$$

Substituting in (4.6) and (4.7)

$$R^S = \tan \alpha$$

$$\overline{OC}^S = 1 - \sec \alpha$$

$$e_{xy}^S = \sin \alpha$$

$$e_{xx}^S = 1 - \cos \alpha$$

$$e_{yy}^S = 1 - \frac{1 + \sin^2 \alpha}{\cos \alpha}.$$
(5.4)

It can immediately be seen that in order to construct Mohr's circles corresponding to Swainger's measure, the centre of the circle should be placed in the negative direction with the same distance from the origin as in the case of Cauchy's measure. The radii in the two cases are the same. It is therefore sufficient to turn the position of the circles drawn for Cauchy's measure by 180° . This is achieved when Figure 5 is turned upside down.

(iv) *Relations between Cauchy's and Swainger's measures*

Comparing (5.3) and (5.4), the following relations can be established.

$$e_{xy}^C = e_{xy}^S$$

$$e_{xx}^C = -e_{yy}^S$$

$$e_{yy}^C = -e_{xx}^S$$
(5.5)

These relations are valid for all cases of simple shear. Relations (5.5) can be proved from (4.7) as follows: —

$$e_{xx}^C = R^C \sin \alpha + \overline{OC}^C = \frac{1}{2}(e_i^C + e_j^C) + \frac{1}{2}(e_i^C + e_j^C) \sin \alpha = \frac{1}{2}(l_i + l_j - 2) +$$

$$+ \frac{1}{2}(l_i - l_j) \sin \alpha = \frac{1}{2}(l_i + l_j) + \frac{1}{2}(l_i - l_j) \sin \alpha - 1;$$

$$\begin{aligned}
 -e_{yy}^S &= -\overline{OC}^S + R^S \sin \alpha = -\frac{1}{2}\left(2 - \frac{1}{l_i} - \frac{1}{l_j}\right) + \frac{1}{2}\left(\frac{1}{l_j} - \frac{1}{l_i}\right) \sin \alpha = \\
 &= \frac{1}{2} \frac{l_i + l_j}{l_i l_j} + \frac{1}{2} \frac{l_i - l_j}{l_i l_j} \sin \alpha - 1
 \end{aligned}$$

and with (5.1), namely $l_i l_j = 1$, the result is

$$e_{xx}^G = -e_{yy}^S.$$

Similar proofs can be derived for the other relations in (5.5). Numerical results for Swainger's measure are shown in connection with those of Cauchy's in Figure 5.

(v) *Green's measure* — e^G .

In accordance with definition (3.3),

$$\begin{aligned}
 e_i^G &= \frac{1}{2}(l_i^2 - 1) = \frac{1}{2} \left[\frac{(1 + \sin \alpha)^2}{\cos^2 \alpha} - 1 \right] \\
 e_j^G &= \frac{1}{2}(l_j^2 - 1) = \frac{1}{2} \left[\frac{(1 - \sin \alpha)^2}{\cos^2 \alpha} - 1 \right]
 \end{aligned}$$

Substitution in (4.6) and (4.7) yields

$$\begin{aligned}
 R^G &= \tan \alpha \sec \alpha \\
 \overline{OC}^G &= \tan^2 \alpha \\
 e_{xy}^G &= \tan \alpha = \frac{\Gamma}{2} \\
 e_{xx}^G &= 2 \tan^2 \alpha = \frac{\Gamma^2}{2} \\
 e_{yy}^G &= 0
 \end{aligned} \tag{5.6}$$

Numerical results are shown graphically in Figure 5.

(vi) *Almansi's measure* — e^A .

From definition (3.4) and equations (4.6) and (4.7), we get

$$\begin{aligned}
 R^A &= \tan \alpha \sec \alpha = R^G \\
 \overline{OC}^A &= -\tan^2 \alpha = -\overline{OC}^G \\
 e_{xy}^A &= \tan \alpha = \frac{\Gamma}{2} = e_{xy}^G \\
 e_{xx}^A &= 0 = -e_{yy}^G \\
 e_{yy}^A &= -2 \tan^2 \alpha = -e_{xx}^G.
 \end{aligned} \tag{5.7}$$

In this case, and in all other cases of simple shear, the relations between e^G and e^A are analogous to those between e^C and e^S . The corresponding diagrams are given in Figure 5.

6. Discussion of Green's measure.

Love² derives a measure which he represents as "the measure of finite strain", starting from Eq. (7), (Art. 24):

$$\frac{1}{2} \left[\left(\frac{ds}{ds_0} \right)^2 - 1 \right] = e_{xx} l^2 + 2e_{xy} lm + e_{yy} m^2. \quad (6.1)$$

The left side is an expression equivalent to our (3.3). He finds for simple shear

$$||e_{rs}||_{x,y} = \left\| \begin{array}{cc} 0 & \Gamma/2 \\ \Gamma/2 & (\Gamma^2/2) \end{array} \right\| \quad (6.2)$$

The right side of (6.1) is the transformation law of a symmetric tensor of the second rank, in other words the principal component expressed through the components in the x, y -directions. Note that in order for e_{xy} to be a tensor component, half of the value of e_{xy} appearing in Love² should be taken in (6.1) and (6.2).

The analysis of simple shear shows us that the principal directions of the deformation ellipse, in their final equilibrium position, denoted by i, j , are inclined towards the x, y -directions by the angles $\beta = \frac{\pi}{4} - \frac{\alpha}{2}$ and $90^\circ + \beta$ respectively. If, however, we restore the body to its original shape by the same amount, the i, j -directions will rotate and occupy the positions \bar{i}, \bar{j} , where the angle of rotation α (Figure 6) is given by (1.5). The latter directions are referred to as the initial directions of the principal axes. Belonging to the unstrained state of the body, they possess no physical significance and are purely geometrical. Bearing in mind that the direction cosines in (6.1)

$$l = \frac{dx}{ds_0} \quad m = \frac{dy}{ds_0},$$

refer to the initial directions of the principal axes, we conclude that (6.1) represents the principal component $e_{\bar{i}\bar{i}}^G$, expressed in terms of the components in the x, y -directions, and (6.1) now reads

$$e_{\bar{i}\bar{i}}^G = e_{xx} l^2 + 2e_{xy} lm + e_{yy} m^2. \quad (6.3)$$

But it is the principal component denoted by e_i^G in the direction of the final-equilibrium principal axes of deformation which we wish to find. The left side of (6.3) is invariant and stands for Green's measure in the principal directions, but the right side should be expressed in terms of the 'final' direction cosines denoted as l', m' . Thus, from Figure 6,

$$l' = \cos \beta \quad m' = \cos(90 - \beta) = \sin \beta,$$

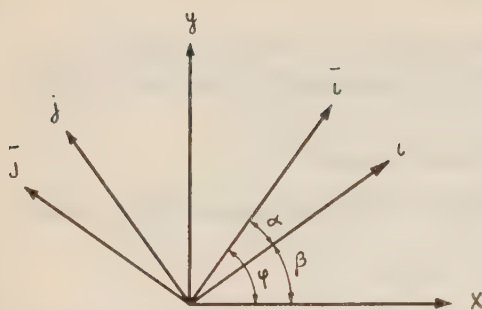


Figure 6
Mutual relation between reference systems x, y ;
 i, j and \bar{i}, \bar{j}
 \bar{i}, \bar{j} principal axes before deformation
 i, j principal directions after deformation

and (6.3) should read

$$e_i^G = \frac{1}{2} \left[\left(\frac{ds}{ds_0} \right)^2 - 1 \right] = e'_{xx} l'^2 + 2e'_{xy} l' m' + e'_{yy} m'^2. \quad (6.4)$$

On substituting

$$l = \cos \varphi = \cos (\alpha + \beta) = l' \cos \alpha - m' \sin \alpha$$

$$m = \sin \varphi = \cos (90 - \alpha - \beta) = m' \cos \alpha + l' \sin \alpha$$

(see Figure 6) into (6.3), and comparing with (6.4), we find the following relations between the e_{rs} and the e'_{rs} :

$$\begin{aligned} e'_{xx} &= e_{xx} \cos^2 \alpha + e_{yy} \sin^2 \alpha + 2e_{xy} \sin \alpha \cos \alpha \\ e'_{yy} &= e_{xx} \sin^2 \alpha + e_{yy} \cos^2 \alpha - 2e_{xy} \sin \alpha \cos \alpha \\ e'_{xy} &= (-e_{xx} + e_{yy}) \sin \alpha \cos \alpha + e_{xy} (\cos^2 \alpha - \sin^2 \alpha). \end{aligned} \quad (6.5)$$

Relations (6.5) are again the transformation formulas of a symmetric tensor of the second rank. Now they imply that if the e_{rs} are found first, they should further be amended by "rotating" them through the angle of rotation α , thus yielding the correct components e'_{rs} of Green's measure with respect to the final equilibrium state of deformation*.

The above discussion and distinction is necessary only when the deformation is not "pure", i.e. when it is accompanied by a rotation as in simple shear. In general Eqs. (6.4) and (6.5) should replace (6.1) and (6.2), when Green's measure is used. It is also evident from (6.5) that in cases of "pure" deformation ($\alpha = 0$), e_{rs} coincides with e'_{rs} .

The graphical method of finding deformation components by means of Mohr's circle allows even for a simpler explanation of the difference in results. If the axis of Mohr's circle is in the direction of the initial principal axis \bar{i} , we obtain Love's results (6.2) for the components e_{rs} in the x, y -directions. If, however, Mohr's circle is constructed along the final principal axis i as should always be done (see Figure 2), we obtain the values e_{rs}^G — Eq. (5.6) for the components in the x, y -directions.

* See also Reiner⁴.

7. Second-order terms in various measures of deformation

Examining the curves in Figures 2, 5, we obtain the following results for the deformation components in the x, y -directions in the five main measures.

(i) *Cauchy's measure.*

The shear component e_{xy}^C -curve shows a deviation from linearity and falls below the linear one. In addition there is also a positive component e_{xx}^C , and a negative component $-e_{yy}^C$. Also $e_{xx}^C > e_{yy}^C$ in magnitude.

(ii) *Swainger's measure.*

Here again the normal components are positive in the x -direction, and negative in the y -direction. The $e_{xy}^S = e_{xy}^C$, and also $e_{xx}^S = -e_{yy}^C$ and $e_{yy}^S = -e_{xx}^C$; hence this time $e_{xx}^S < e_{yy}^S$ in absolute magnitude.

(iii) *Hencky's measure.*

This is the only measure for which $e_{xx}^H = -e_{yy}^H$, and hence the first invariant vanishes in magnitude. There is again a positive component in the x -direction and a negative one in the y -direction. The relation between Γ and e_{xy}^H is again non-linear but of a magnitude different from those in the two preceding measures.

(iv) *Green's measure.*

Here a positive component only exists in the x -direction, while in the y -direction the strain equals zero. The relation $e_{xy}^G = e_{xy}^G(\Gamma)$ is linear. Hence Hooke's law for the shear stress

$$\tau_{xy} = 2G e_{xy}$$

is valid with Green's measure also for finite elastic simple shear as well as for the infinitesimal deformation.

(v) *Almansi's measure.*

There is no strain component in the x -direction and there exists a negative component of the amount $e_{yy}^A = e_{xx}^G$ in the y -direction; e_{xy}^A is equal to e_{xy}^G . Again there exists a linear relation for the function $e_{xy}^A = e_{xy}^A(\Gamma)$.

CONCLUSIONS

To sum up the various results discussed above, the following important properties of the various measures should be noted:—

A common property for all measures is the very fact of existence of normal strain components e_{xx} , e_{yy} in directions of the shearing displacement and normal to it respectively. This is a property which is not found in classical theory, which regards the e_{xx} and e_{yy} as zero. As no quantity can be neglected in comparison with zero, however small it may be, we conclude that normal strain components e_{xx} , e_{yy} manifest themselves in simple shear and in any of the five measures, although they are second-order terms.

For all measures there is a positive strain component in the x -direction (with the particular case $e_{xx}^A = 0$), and a negative component in the y -direction (with the particular case $e_{yy}^G = 0$).

Hencky's measure is the only one for which $e_{xx} = -e_{yy}$, a well-known relation which exists in pure shear between the principal strains inclined to the shear strain by 45° . Hencky's measure is related to all intermediate stages passed by the body from the initial to the final state. On the other hand there is no linear relation $e_{xy} = e_{xy}(I)$.

Almansi's measure is related to the final equilibrium state of the body. The linear relation between e_{xy} and I is retained, and furthermore this is the only measure for which $e_{xx} = 0$. This has an interesting implication, mentioned above in Section 2. From an inspection of Figure 2 we see that, due to the shear, no change in length of a line element in the x -direction takes place. Intuition might therefore demand that no deformation be in this direction. It is only Almansi's measure which satisfies this view while others yield an e_{xx} -component different from zero.

□

ACKNOWLEDGMENT

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A SENSITIVE TWO-LIQUID MICRO-MANOMETER

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The ordinary water or alcohol U-tube manometer is a simple and efficient tool for the measurement of air speed in low-speed wind tunnels. The usual requirement of a minimum speed in the wind tunnel test section of about 50 m/sec is mainly dictated by the sensitivity of such manometers. Assuming an air density of $0.125 \text{ kg sec}^2/\text{m}^4$ and a water density of $100 \text{ kg sec}^2/\text{m}^4$, the dynamic pressure of an air stream of 50 m/sec is indicated by a level difference of 15.6 cm in a water U-tube manometer.

Since this level difference varies in proportion to the square of velocity, the instrument becomes quite insensitive at lower velocities.

Many ingenious devices have been developed in order to improve the sensitivity of manometers at low speed. Some typical examples of such micromanometers are the Betz manometer, the Prandtl manometer, the Chattock gauge and the inclined tube manometer. Their detailed description may be found in any textbook on the subject (see e.g. refs. 1 and 2). Each one of these devices has its own merits as well as limitations with respect to sensitivity, accuracy, simplicity and ease of handling.

The following is a description of a simple yet quite sensitive micro-manometer developed at the Aerodynamics Laboratory of the Technion-Israel Institute of Technology.

The manometer consists of a U-tube with branches built of tube segments of different diameters (Figure 1). The diameter d_1 of the upper tubes is much larger than the diameter d_2 of the lower ones. The tubes are filled with two immiscible liquids of different colours and of densities ρ_1 and ρ_2 . A small displacement of the free surfaces under the influence of a pressure differential will be accompanied by a much larger displacement of the interface in the small-diameter tube.

Suppose that under zero pressure differential, the free surfaces of the liquids are at heights h_1 and h_2 above the interface. The condition of hydrostatic equilibrium is given by the equation

$$\rho_1 h_1 = \rho_2 h_2 \quad (1)$$

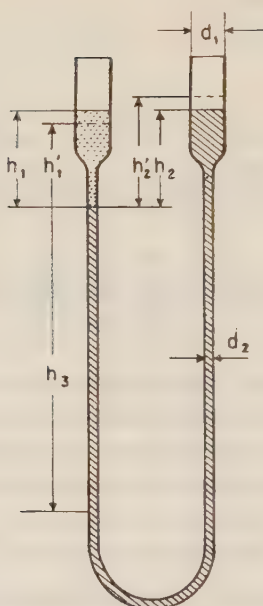


Figure 1
Two-liquid micro-manometer

When a pressure differential $\Delta p = p_1 - p_2$ is applied at the free surfaces, one of them is depressed to the height h_1' and the other one is raised to the height h_2' . The interface is depressed by a distance h_3 . The new equilibrium condition is expressed by

$$\Delta p + g\varrho_1(h_1' + h_3) = g\varrho_2(h_2' + h_3) \quad (2)$$

The condition of incompressibility of the liquid and the principle of the conservation of mass supply two relations between h_1 , h_2 , h_3 , h_1' and h_2'

$$(h_1 - h_1') d_1^2 = (h_2' - h_2) d_2^2 = h_3 d_2^2$$

or

$$h_2' - h_2 = -(h_1' - h_1) = \left(\frac{d_2}{d_1}\right)^2 h_3 \quad (3)$$

Subtracting Eq. (1) from Eq. (2) and then substituting for $h_1' - h_1$, and $h_2' - h_2$ from Eq. (3), we obtain

$$\Delta p = \left[(\varrho_2 - \varrho_1) + \left(\frac{d_2}{d_1}\right)^2 (\varrho_1 + \varrho_2) \right] g h_3 \quad (4)$$

Define the manometer "sensitivity" factor K by the following equation:

$$K = \frac{1}{\left(\frac{\varrho_2 - \varrho_1}{\varrho_2 + \varrho_1}\right) + \left(\frac{d_2}{d_1}\right)^2} \frac{1}{(\varrho_2 + \varrho_1) g} \quad (5)$$

Then Eq. (4) becomes

$$h_3 = K \Delta p \quad (6)$$

Let \bar{K} be the "sensitivity" of an ordinary U-tube manometer with $d_2 = d_1$, when filled with the same two liquids of densities ϱ_1 and ϱ_2 . Let \bar{h}_3 be the displacement of its interface under the same pressure differential Δp . By Eqs. (5) and (6) we obtain

$$\bar{K} = \frac{1}{1 + \frac{\varrho_2 - \varrho_1}{\varrho_2 + \varrho_1}} \frac{1}{(\varrho_2 + \varrho_1)g}$$

and

$$\bar{h}_3 = \bar{K} \Delta p$$

Defining the manometer amplification factor M as the ratio h_3/\bar{h}_3 , we obtain

$$M = \frac{1 + \left(\frac{\varrho_2 - \varrho_1}{\varrho_2 + \varrho_1} \right)}{\left(\frac{d_2}{d_1} \right)^2 + \left(\frac{\varrho_2 - \varrho_1}{\varrho_2 + \varrho_1} \right)} \quad (7)$$

For a given diameter ratio $(d_2/d_1) < 1$ the amplification factor M increases with decreasing relative density difference $(\varrho_2 - \varrho_1)/(\varrho_2 + \varrho_1)$. It is therefore convenient to choose two liquids with a relative density difference as small as possible.

Once the manometer liquids are chosen it is seen from Eq. (7) that the amplification increases with decreasing d_2/d_1 . In the limit it tends to its maximum value

$$M_{\max} = \frac{2}{1 - (\varrho_1/\varrho_2)} \quad (8)$$

Figure 2 is a plot of the amplification factor M vs (d_2/d_1) for different values of the density parameter $(\varrho_2 - \varrho_1)/(\varrho_2 + \varrho_1)$.

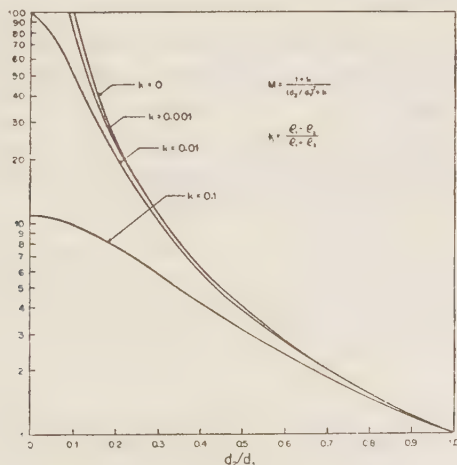


Figure 2

The two liquids used with the manometer should fulfill the following requirements: They must be immiscible, their densities should be as close as possible and they should be of low viscosity. It is also desirable that they should have different colours or there should be a possibility to dye one of them by some substance that is not attacked chemically or dissolved by the other liquid.

In the present version the liquid media were kerosene and ethyl alcohol. The alcohol was diluted with water, the density of the solution being $\rho_2 = 0.813 \text{ g/cm}^3$. The density of kerosene is $\rho_1 = 0.795 \text{ g/cm}^3$. Thus the relative density difference of the system is

$$\frac{\rho_2 - \rho_1}{\rho_2 + \rho_1} = 0.0112.$$

With a tube diameter ratio $(d_2/d_1) = 0.119$ (the tubes used were Jobling precision through-bore tubes of diameters $5 \pm 0.02 \text{ mm}$ and $42 \pm 0.05 \text{ mm}$), a nominal amplification $M = 39.8$ was obtained.

It should be noted that the effective amplification of sensitivity of the manometer when compared with a common U-tube single liquid manometer is about half the value calculated above. This is explained by the fact that in the common manometer the pressure is measured by the difference in free-surface level in the two branches of the U-tube, and not by the mere depression of one of them.

The manometer amplification can be improved in this respect by the introduction of the following change: The lower part of the U-tube could be filled with alcohol and the two upper parts of its branches with kerosene. Two interfaces between alcohol and kerosene would thus be established, and their relative displacement in response to a pressure difference would be twice the displacement of each interface.

But such an arrangement would require two readings for each pressure measurement. Besides the added complication, this would reduce the real gain in sensitivity by introducing another source of error.

In conclusion the author would like to express his gratitude to Mr. E. Nissim and Mr. M. Victor for their help in the development of the instrument.

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NON-ENZYMATIC BROWNING IN COMMERCIAL GLUCOSE SYRUPS

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ABSTRACT

This study deals with a number of factors affecting the colour of glucose syrups on storage: the origin of the raw material, its protein content, the final pH of the syrup, and treatment with activated carbon.

INTRODUCTION

The browning of commercial glucose syrups, occurring occasionally immediately after preparation and frequently during storage, is of great interest to the manufacturer. Although a number of papers on the subject have been published, the final solution to the problem has not yet been found.

Browning of glucose syrup may be due to one of the known browning reactions of carbohydrates: (1) the Maillard reaction, (2) interactions other than between sugars and NH_2 groups. Both processes are initiated by enolisation and involve the formation of highly reactive intermediates, such as furfural, hydroxymethylfurfural, methylglyoxal, reductones, products of dehydration, etc.²⁰

What is generally called the "Maillard reaction" is the darkening of sugars caused by the interaction with amino-acids. In the case of glucose syrups, it is directly dependent on their N-content^{6,15}, the amino-acids being formed from protein during starch hydrolysis. Light and ultraviolet radiation have been shown to have no influence on this type of browning^{6,7}. Copper ions accelerate the reaction⁷ and SO_2 has a retarding effect. The Maillard reaction has been shown to accelerate with increase of temperature and pH.

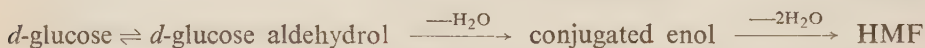
It should be understood that the term "Maillard reaction" comprises more than one reaction. A comprehensive paper by Hodge¹⁹ gives a general scheme of the reactions involved.

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Where no amino group is present, the Amidori rearrangement of the Maillard reaction may—in an alkaline medium—be replaced by that of Lobry de Bruyn–van Ekenstein. In neutral solutions, however, glucose may be converted also into reductones on prolonged storage at ordinary temperatures, while the reductones in turn may be converted into melanoidines, as in the case of ascorbic acid.

Special attention was drawn by several authors (Deschreider, Lindemann) to the formation of 5-hydroxymethylfurfural (HMF) as an intermediate during browning of commercial glucose (demonstrated in model systems subjected to heat^{12,13}). According to Lindemann^{7,8} HMF is found in commercial samples; it disappears under the influence of light and seems not to be present in syrups on prolonged storage.

Wolf from et al.¹⁶ proposed the following scheme for the formation of HMF from glucose:



In commercial syrups 10 to 80 mg of HMF per kg syrup may be found, and while the amount of HMF formed is directly proportional to the dextrose concentration, the rate of the reaction is of zero order, i.e. independent of the concentration of the reactants. Increased temperature accelerates the formation of HMF^{6,7,8}, thus causing an increase in the rate of browning, although the HMF concentration in itself has no direct relationship to the intensity of colour. Acidity has a marked influence on the formation of HMF⁸; at pH 3 the browning of heated syrups is at a minimum^{2,13}.

As for amino-acids, not all of them have the same effect on browning. While leucine has been shown to have no effect on colour formation¹³, others, such as aspartic acid, react readily with an aldehyde such as HMF.

The material of which the convertor is constructed may also be a factor affecting the browning process. This has been studied by several authors^{1,6,7} who showed that copper present in amounts of 10 ppm or higher accelerates browning. Larger amounts may cause an off-colour or turbidity, due to the formation of insoluble compounds.

Finally, the degree of browning depends on that of starch hydrolysis, i.e. the dextrose equivalent (D.E.)¹⁵.

The present study deals with a number of factors likely to affect the colour of the glucose syrups on storage, namely, the origin of the raw material, its protein content, the final pH of the syrup, and treatment with activated carbon.

Methods employed

1. Ultraviolet spectra of the syrups were analysed by means of a DU model Beckmann spectrophotometer. The amount of HMF formed can easily be measured, since its ultraviolet spectrum has a definite minimum at $\lambda = 245 \text{ m}\mu$ and two maxima at $284 \text{ m}\mu$ (or $282.5 \text{ m}\mu$) and at 228 to $230 \text{ m}\mu$ ¹⁴. Glucose syrups do not show this

last maximum at pH 2–5 because of the conjugated enol of the intermediate compounds masking it^{1,12,13}. The total HMF content is, therefore, determined from the difference between the respective 245 m μ and 284 m μ absorption coefficients⁷.

2. Visible colour was measured by means of a Gallenkamp colorimeter with violet filter No. 621.

3. Protein content was determined according to Lindemann⁹, with the aid of the Kjeldahl and Nessler apparatus. For the soluble protein content, 250 g starch were washed with 10 l. of distilled water on a Buchner funnel and the protein was determined in the filtrate as above.

4. Phosphates were determined by methods adapted by the A.O.A.C.

5. Dextrose equivalents were determined by the polarimetric method of Wolff¹⁷.

EXPERIMENTAL

Syrups were prepared from *potato starch* (0.095% protein, all soluble), and *sorghum starch* ("Milocorn", 1.02% protein, but only 0.009% soluble). Supplementary soluble protein, when added, was derived from the gluten water of the cornstarch production.

Five series of 40% starch suspensions were prepared with different amounts of added proteins, with or without the addition of activated carbon and phosphates, as shown in the list below. To these, concentrated HCl was added to bring their pH to 1.8. The starch suspensions were hydrolysed in an autoclave at 2.4 atm until a conversion of 55% D.E.* was attained. (The relatively high D.E. was chosen in order to obtain accelerated browning in the given storage time). The syrups obtained were adjusted to pH 5 and, after addition to some of them of activated carbon (Gluconorit No. 2), filtered on a Buchner funnel, using Whatman No. 1 filter paper. All syrups, with and without activated carbon, were concentrated in vacuo at 50°C to 60°Bx. After further addition of activated carbon and filtration, the pH of the various syrups was adjusted as above and all samples were further concentrated in vacuo to 85°Bx.

All samples were kept in the dark for 33 days at 30°C, another 4 days at 50°C, a further 18 days at 30°C, and finally 5 days at 50°C. Storage at 50°C was undertaken with a view to accelerating the reactions taking place at room temperature.^{7**}

The following were the five series of 40% starch suspensions prepared:

Series 1 (9 samples, No. 1.21 to 1.29 and 1.05). Potato starch with 0.2% phosphate. No. 1.21 to 1.29 (pH 1, 2, 3, 4, 5, 6, 7 and 9 respectively) treated with 2% and 5% activated carbon; No. 1.05 (pH 5) untreated.

Series 2 (1 sample, No. 2.25, pH 5). As above, treated with 7% and 5% carbon.

Series 3 (3 samples). As above, plus additional 0.11% soluble cornstarch protein. No. 3.05, untreated; No. 3.15, 0.7% and 1.3% carbon; No. 3.25, twice 5% carbon.

* Corresponding to approximately 51% D. E. by the reducing sugar method.

** The influence of SO₂ was not dealt with in the present study.

Series 4 (2 samples). As above, plus additional 0.22% soluble cornstarch protein. No. 4.05, untreated; No. 4.25, 5.5% and 5% carbon.

Series 5 (11 samples). Sorghum starch (1.18% total protein, 0.01% soluble) plus additional 0.16% soluble cornstarch protein. No. 5.01 to 5.09 (pH 1, 2, 3, 4, 5, 6, 7 and 9 respectively), untreated; No. 5.15, 0.7% and 1.3% carbon; No. 5.25, 4% and 5% carbon.

RESULTS AND DISCUSSION

Visible colour measurements were taken in a colorimeter at appropriate intervals, the results being given as extinction coefficients of a 50% solution, $\epsilon^{50\%}$ or $\epsilon_{420\text{ m}\mu}$. The ultraviolet readings were calculated for a 5% solution and given as $\epsilon^{5\%}$. The difference of the respective values for 285 m μ and 245 m μ ($\epsilon_{285\text{ m}\mu}^{5\%} - \epsilon_{245\text{ m}\mu}^{5\%}$) was the measure of the HMF content.

The changes over the period of exposure are summarised in Tables I and II and the diagrams in Figures 1, 2.

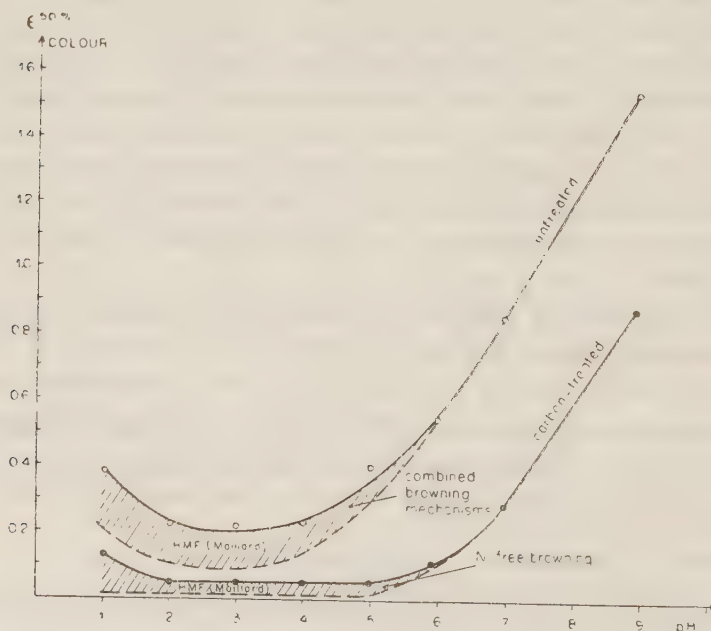


Figure 1

Colour and HMF content over the testing period

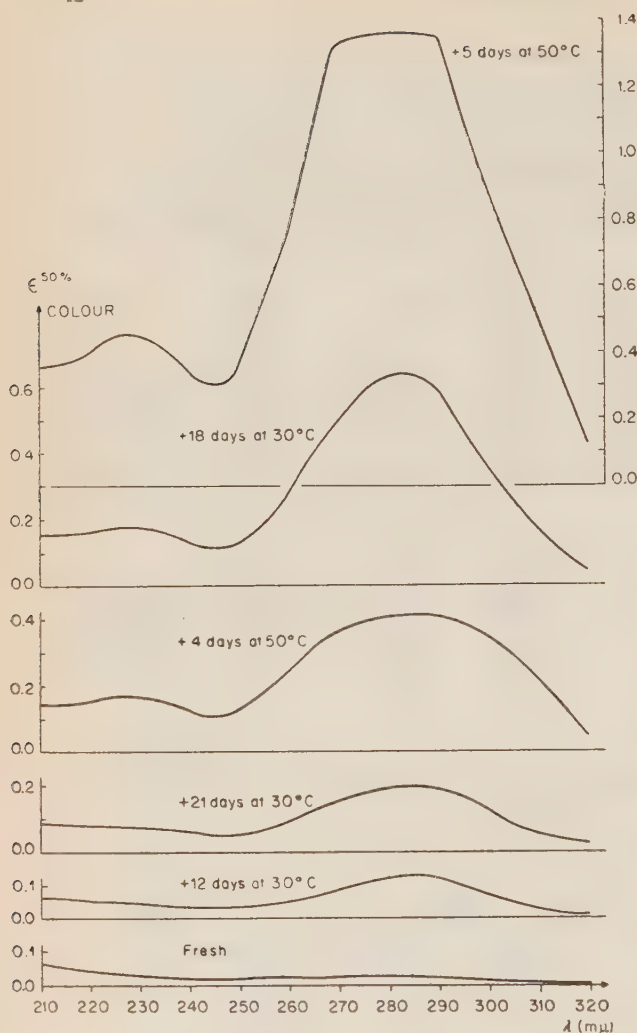
TABLE I
HMF content in glucose syrups
(given as difference of extinction coefficients $\epsilon_{285\text{ m}\mu}^{5\%} - \epsilon_{245\text{ m}\mu}^{5\%}$)

Sample	pH	Time of exposure					REMARKS
		Initial value	12 days at	After additional			
			30°C	21 days at 30°C and 4 days at 50°C	18 days at 30°C	5 days at 50°C	
5.01	1	0.661	0.716	1.042	1.155	1.839	Untreated
5.02	2	0.693	0.676	0.757	1.046	1.127	
5.03	3	0.634	0.673	0.913	0.838	0.984	
5.04	4	0.624	0.600	0.832	0.885	0.933	
5.05	5	0.637	0.597	0.700	0.776	0.857	
5.06	6	0.626	0.582	0.570	0.682	0.725	
5.07	7	0.540	0.451	0.361	0.520	0.447	
5.09	9						
U. V. spectral show maxima at 270 mμ and minima between 245–260 mμ							
1.21	1	0	0.090	0.300	0.518	1.054	Treated with 10% activated carbon
1.22	2	0	0	0.054	0.063	0.142	
1.23	3	0	0	0.035	0.045	0.083	
1.24	4	0	0	0.036	0.047	0.122	
1.25	5	0	0	0.025	0.031	0.097	
1.26	6	0	0	0	0	0.011	
1.27	7	0	0	0	0		
1.29	9	0	0				
U. V. spectra show minute differences between maxima and minima uncharacteristic for HMF							

TABLE II
Extinction coefficients $\epsilon^{50\%}$ over visible range

Sample	pH	Time of exposure				REMARKS
		Initial value	33 days at 30°C	4 days at 50°C	After additional 18 days at 30°C 5 days at 50°C	
5.01	1		0.270	0.342	0.334	Untreated
5.02	2		0.200	—	—	
5.03	3		0.161	0.204	0.197	
5.04	4	Not determined	0.162	0.196	0.203	
5.05	5		0.240	0.286	0.296	
5.06	6		0.274	0.360	0.412	
5.07	7		0.444	0.518	0.561	
5.09	9		1.011	1.180	1.242	
1.21	1	0.040	0.043	0.062	0.067	Treated with 10% activated carbon
1.22	2	0.033	0.038	0.050	0.048	
1.23	3	0.038	0.038	0.043	0.046	
1.24	4	0.036	0.040	0.044	0.045	
1.25	5	0.042	0.043	0.050	0.048	
1.26	6	0.031	0.036	0.063	0.067	
1.27	7	0.041	0.097	0.212	0.191	
1.29	9	0.121	0.430	0.701	0.641	

Limit extinction coefficient visible to the naked eye — 0.047–0.050.



Maximum and minimum wavelengths

Time	Max (mμ)	Min (mμ)
0	275 — 280	245 — 248
+ 12d. at 30°C	282 — 286	247
+ 21d. at 30°C	284	246
+ 4d. at 50°C	230 285 — 290	245
+ 18d. at 30°C	228 — 229	245
+ 5d. at 50°C	227 283	245

Figure 2

U. V. spectrum, Series 1 (treated), pH 1

The influence of pH

The samples of Series 1, containing only a small amount of protein and treated with activated carbon, showed no colour at the outset ($\epsilon^{50\%} = 0.050$) and no HMF or any visible colour at pH 2–4. At pH 1, however, there was some browning, and from pH 6 upwards the browning was very intensive (the usual effect with sugar).

HMF formed only on storage; at pH 1 it began to form almost from the outset and its content increased with time (Figure 2), while at higher pH it began to form much later. At pH 6 a small amount of HMF seemed to form in the final stages

of the experiment; at pH 7–9 a small difference between maximum and minimum in the vicinity of the above wavelengths could be observed towards the end of the storage period, indicating either the absence of HMF or its masking by another substance.

In contrast to the above, the samples of Series 5 contained a comparatively large amount of protein (0.23%). All the samples contained HMF (Table I) and were coloured from the outset (Table II). Here also the colour curve showed a minimum at pH 3 towards the end of the experimental period, a sharp rise towards the alkaline range and a moderate rise towards the acid range (Figure 1).

Curves correlating the amounts of colour and HMF are given in Figures 3 and 4. A clear-cut dependence could only be observed on elevating the storage temperature to 50°C, which led also to increased reaction rates, mainly in the formation of HMF. At the same time it could be seen that the samples with lower protein content and pH tend more to HMF formation than those with higher pH and protein levels. Figure 4 shows a gradual decrease in HMF formation between pH 2–5, as compared with the high level at pH 1. The decrease is intensified at still higher pH levels, so that at pH 7 the process is practically arrested and the HMF content begins to decrease (Table I). At pH 9 the maximum of the ultraviolet spectrum is at 270 mμ instead of 285 mμ; the colour intensity is highest at this pH.

Considering all the above, the following reactions are most likely to be involved:

1. At pH 1, HMF is formed under the influence of the free H-ions and then partially converted, with or without the intervention of amino-groups, into coloured compounds. This, of course, occurs not only on storage, but more explicitly during starch hydrolysis.
2. With increasing pH, the rate of HMF formation is gradually exceeded by that of its conversion, giving rise to intensified browning.
3. At the higher pH levels this reactions replaced by another, probably beginning with the enolisation of glucose or the formation of reductones.

An illustration of the above is given in Figure 1, in which the colour and HMF contents are shown at the end of the experimental period.

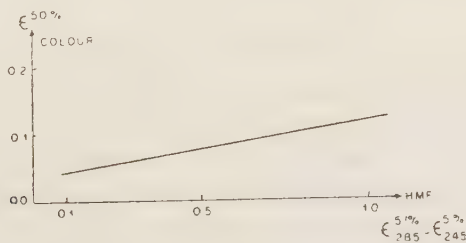


Figure 3
HMF content vs. colour (treated)

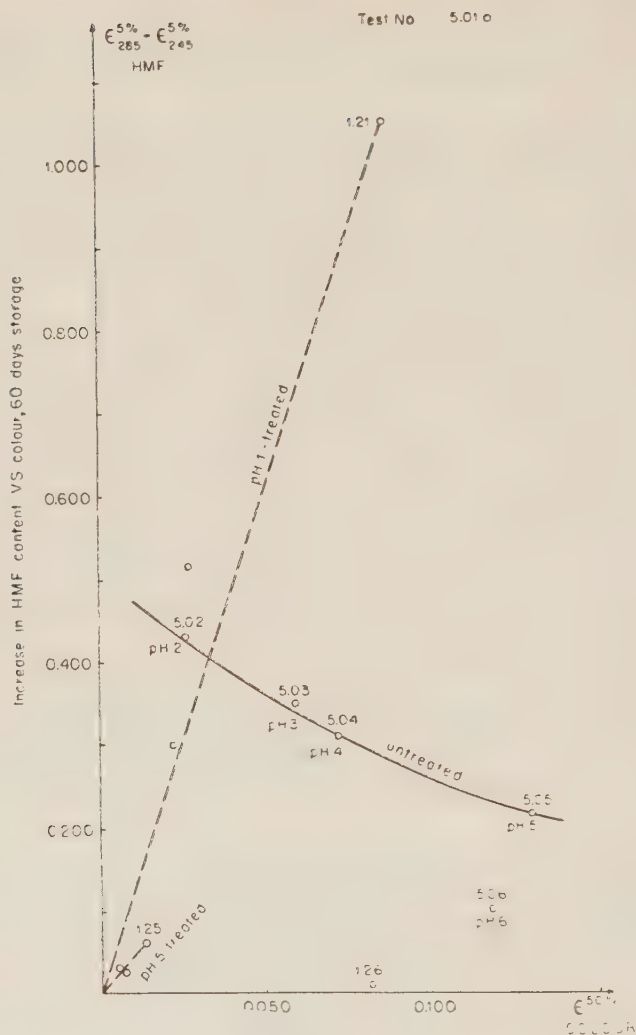


Figure 4

The influence of protein

It has been confirmed that the visible colour and HMF are mainly related to the amount of water-soluble protein, not the total protein (Table III).

During industrial acid hydrolysis of starch (at pH 1.5–2.0 and about 140°C), insoluble proteins are attacked to a lesser degree than water-soluble ones. On neutralisation, the bulk of the former is precipitated and eliminated by filtration, while the latter—mostly degraded to amino-acid level—remain in the liquor and are responsible for the changes taking place on storage.

A close relationship seems to exist between protein content, browning and HMF content. The behaviour of carbon-treated syrups is similar to that of untreated syrups at corresponding N-levels (Figure 5).

The syrups prepared from sorghum starch, with corn gluten water added in order to raise the soluble protein content, show slightly different characteristics. The HMF content is lower and colour formation slower than in other samples with the same N-content. This may be due to the difference a composition of the sorghum protein as compared with the corn and potato proteins. As already reported¹³, amino-acids do not all have the same effect on the browning mechanism. This, together with the

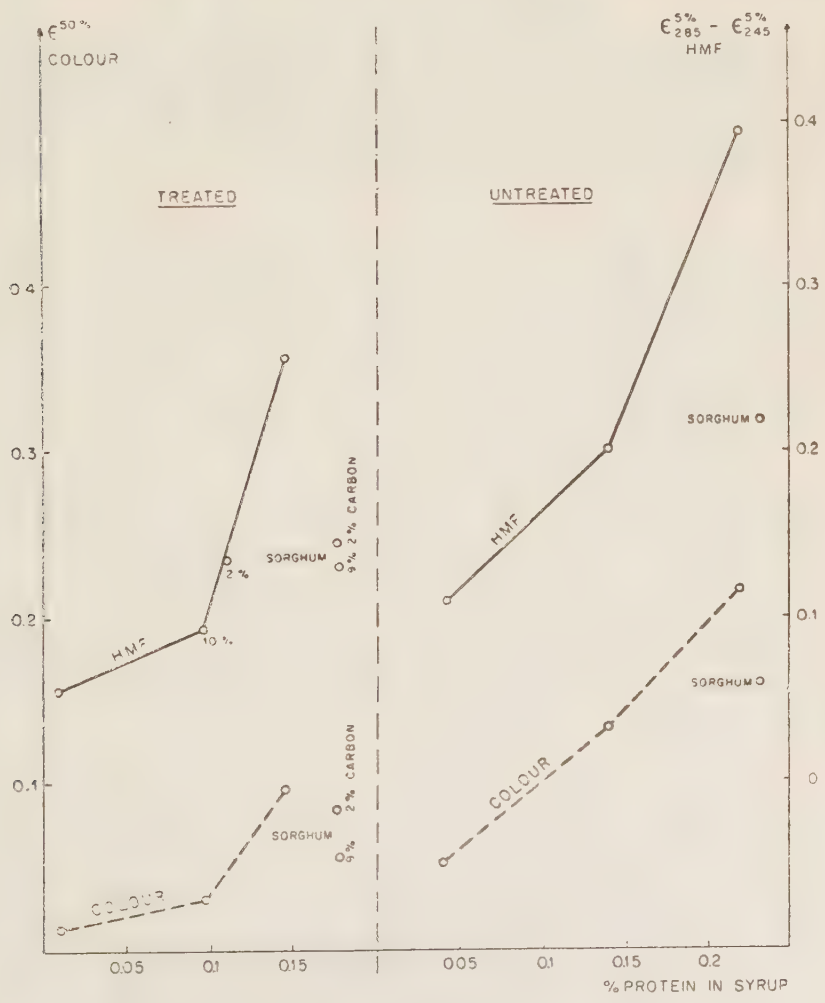


Figure 5
Colour and HMF increase vs. protein content, 60 days storage

fact that it is the soluble starch protein which is mainly retained in the glucose syrup, accounts for the superior quality, as far as darkening is concerned, of the samples of Series 5 (prepared from sorghum, 1.18% protein, only 0.17% soluble) when compared with those of Series 4 (prepared from potato starch, with a total protein content of 0.31%, most of it soluble) (Table III).

As a practical point it might be suggested that sorghum starch with a total protein content as high as one percent, but only 0.01–0.03% soluble, is safer to use in glucose syrup manufacture than, say, cornstarch, with much less total protein but up to 0.07% soluble.

The influence of carbon treatment

This is seen clearly in Figure 6. Untreated syrups show the characteristic ultraviolet spectra of HMF, while those filtered after treatment indicate no presence of HMF. There is also ample evidence (see Table IV) that the activated carbon absorbs nearly all of the colour as well as part of the proteins present.

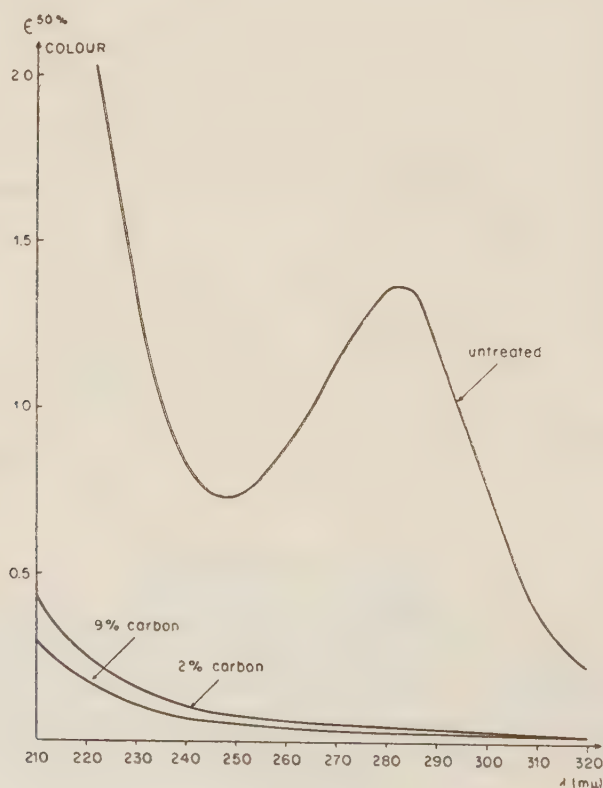


Figure 6
U. V. spectrum, Series 5, pH 5

The influence of protein

A. Untreated

Sample	Total protein in starch d. b. %	Protein in syrup (theoretical)		Protein in potato starch syrup %		Initial value 33 days at 30°C		Colour given as $\epsilon^{50\%}$ After 4 days at 50°C		HMF $\epsilon^{5\%}_{285}$ — $\epsilon^{5\%}_{245}$ Initial value After 33 days at 30°C + 4 days at 50°C		REMARKS
		Total %	Added protein (soluble) %	Protein in syrup (experi- mental) %	Protein in syrup (experi- mental) %	Initial value 33 days at 30°C	After 4 days at 50°C	18 days at 50°C	5 days at 50°C	Initial value 30°C + 4 days at 50°C	After 33 days at 18 at 30°C 5 at 50°C	
1.05	0.095	0.04	—	0.04	0.04	0.073	0.095	0.125	0.577	0.774	0.686	Potato starch
3.05	0.20	0.04	0.11	0.15	0.14	Not deter- mined	0.139	0.272	0.530	0.566	0.732	Potato starch + gluten
4.05	0.31	0.04	0.22	0.26	0.22		0.180	0.397	0.577	0.672	0.983	
5.05	1.18	—	0.16 0.01*	0.17	0.23	0.240	0.286	0.400	0.637	0.700	0.857	Sorghum starch + gluten

* Soluble protein in sorghum starch

B. Treated with activated carbon

HMF increase during the experiment given as $\epsilon^{5\%}_{285}$ — $\epsilon^{5\%}_{245}$											
1.25	0.095	0.009	0.042	0.043	0.050	0.056	0.097				Potato starch
3.25	0.20	0.10	0.042	0.048	0.064	0.079	0.094				Potato starch + add.
4.25	0.31	0.15	0.043	0.050	0.074	0.148	0.259				Potato starch + add.
5.25	1.18	0.18	0.045	0.053	0.059	0.110	0.131				Sorghum starch + add.

The limit extinction coefficient visible to the naked eye is 0.047 — 0.050.

TABLE IV
The influence of activated carbon treatment

Sample No.	Series	Carbon %	Protein in syrup %	Colour after 60 days	HMF increase
1.25	Potato	7.0	0.009	0.056	0.097
1.05	starch	—	0.04	0.125	0.109
3.25	Potato	10.0	0.097	0.079	0.094
3.15	starch	2.0	0.110	0.126	0.135
3.05	+gluten	—	0.140	0.272	0.202
4.25	Potato starch +gluten	10.5	0.145	0.148	0.259
5.25	Sorghum	9.0	0.178	0.110	0.131
5.15	starch	2.0	0.177	0.143	0.147
5.05	+gluten	—	0.233	0.400	0.220

It can also be seen that the activated carbon treatment inhibits the formation of both HMF and colour on storage in proportion to the amount of carbon used. As mentioned, no colour and no HMF could be observed in freshly treated samples. On storage, samples treated with less carbon are darker and show a higher HMF content; the action of the additional carbon, however, is much less intensive: the inhibitory effect obtained by 10% carbon is at best 25% more efficient than that of five times less carbon.

In the light of the data in Figure 5, it is unlikely that the lesser degree of darkening in syrups treated with more carbon is due to partial absorption of the amino-acids. In the case of sorghum syrups there is a marked difference in colour and HMF content between the two carbon levels, the N-content being the same. This implies the existence of an unidentified substance with catalytic or similar properties, which can be eliminated by increased amounts of carbon.

Incidentally, the economic limit for the use of carbon is 1.5%, based on the dry matter in the syrup.

The influence of phosphates and metals

The presence of phosphates caused no catalytic effect with regard to the formation of colour, nor can any influence be attributed to copper, since parallel tests carried out in glass, copper and stainless steel convertors showed no appreciable differences between results.

Finally, Figure 7 shows an interesting relationship between visible colour and total absorption in the ultraviolet region: the stronger the darkening, the higher the entire spectral curve, implying that browning involves the formation of compounds capable of absorbing ultraviolet light throughout the spectrum.

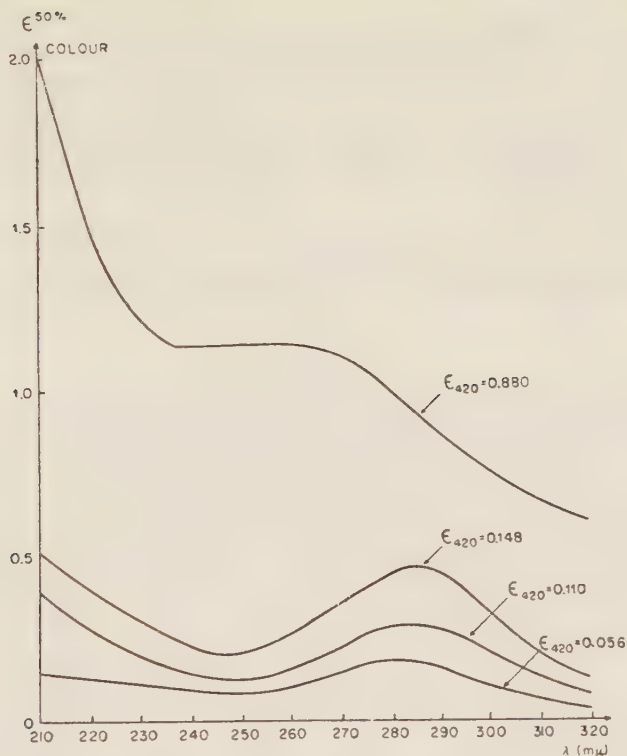


Figure 7
Visible colour vs. total U. V. absorption

CONCLUSIONS

1. The process of conversion of starch into glucose and other carbohydrates by acid hydrolysis is always accompanied by the formation of HMF and subsequent browning. A similar reaction takes place on storage at pH 1.

2. The bulk of the starch protein is eliminated by precipitation. Part of the remaining soluble protein, as well as practically all of the colour formed during hydrolysis and the HMF, are absorbed by activated carbon.

3. At pH 2-5 browning is accompanied by the formation of HMF, which decreases with increasing pH. The colour is at minimum at about pH 3 and intensifies gradually with increasing pH; at pH 5-6 the formation of HMF is arrested. This is explained by the rate of HMF formation being gradually exceeded by that of its conversion leading to a Maillard reaction.

4. At pH 5 and a given D. E., i.e. under the practical conditions of manufacture but in the absence of SO₂, browning on storage depends primarily on the protein content and also on the amino-acid composition of the proteins, as shown

by the behaviour of sorghum glucose versus corn glucose. The protein content of the syrup, in turn, depends almost exclusively on the content of *soluble proteins* in the starch used. N-content, HMF formation and browning are inter-related.

5. With increasing pH the browning reaction is accompanied or replaced by mechanisms not based on the presence of amino-groups, such as enolisation or formation of reductones.

6. No influence on the formation of colour can be attributed to phosphates.

7. Copper and stainless steel showed no effect on browning under test conditions.

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A SHORT NOTE ON THE CONDITIONS FOR MAXIMUM SENSITIVITY OF THE D.C. WHEATSTONE BRIDGE

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ABSTRACT

The conditions for maximum sensitivity of the D.C. Wheatstone bridge are well known. They are: unity ratio of two bridge arms, matching of the resistances of the galvanometer and the outer circuit and positioning of the galvanometer between the junction of the high resistance arms and the junction of the low resistance arms.

It is shown that all these conditions can be obtained by one simple extremum calculation and an extremum calculation with subsidiary condition. As a point of departure it is assumed that the galvanometer should work at critical damping. Furthermore the calculation is made for one single type of galvanometer. This means that the usual assumption is made that the current sensitivity of the galvanometer is proportional to the root of the galvanometer resistance.

The sensitivity calculations for a D.C. Wheatstone bridge are well known, and the following is intended only to show that these calculations may be made in a simpler and more straightforward manner. As a point of departure we take the condition that the galvanometer should operate near its critical damping. For the sake of greater simplicity, the resistance of the battery is neglected. The signs used are explained by the wiring diagram of a simple bridge.

x, r, a, b —resistances of the bridge arms

g —resistance of the galvanometer G

We introduce the ratios:

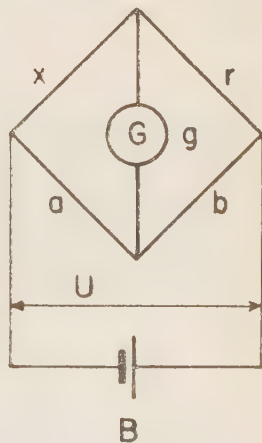
$$\frac{r}{x} = \eta; \frac{a}{x} = \lambda; \frac{g}{x} = \kappa$$

At balance we have $\frac{b}{x} = \eta\lambda$.

Proceeding in the usual way we first find the current through the galvanometer and its change for a small change of x by dx near balance.

The current i_g through the galvanometer is given by:

$$i_g = U \cdot \frac{bx - ar}{g(x + r)(a + b) + xr(a + b) + ab(x + r)} \quad (1)$$



and for its change with dx we find:

$$\frac{\partial i_g}{\partial x} = U \cdot \frac{b}{g(x+r)(a+b) + xr(a+b) + ab(x+r)} \quad (2)$$

$i_g \rightarrow 0$

In order to fulfil the condition that the galvanometer should work at critical damping, we write $R_c = g + R_u$, where R_c is the resistance of the whole circuit for critical damping and R_u the resistance of the bridge arms measured by the galvanometer with the battery replaced by a short circuit:

$$R_u = \frac{xr(a+b) + ab(x+r)}{(a+b)(x+r)} \quad (3)$$

Thus we may write equation (2) as follows:

$$\frac{\partial i_g}{\partial x} = U \cdot \frac{b}{(g + R_u)(x+r)(a+b)} \quad (4)$$

For the relation $\frac{R_c}{g}$ we now introduce the letter n and write for equation (4):

$$\frac{\partial i_g}{\partial x} = U \cdot \frac{b}{ng(x+r)(a+b)} \quad (5)$$

For a finite change of i_g we find:

$$\Delta i_g = U \Delta x \frac{b}{ng(x+r)(a+b)} \quad (6)$$

or by using the above mentioned ratios η , λ , κ :

$$\Delta i_g = \frac{U}{X} \cdot \frac{\Delta x}{X} \cdot \frac{\eta}{n\kappa(1+\eta)^2} \quad (7)$$

As we are interested in the maximum deflection we have to take into account that the current sensitivity $S_i = \frac{\partial \alpha}{\partial i_g}$ is proportional to \sqrt{g} if the induction in the air gap, the spring constant, the moment of inertia, the cross section and the space factor of the coil are constants and α is the deflection of the galvanometer.

Therefore we obtain:

$$\Delta \alpha = S_i \Delta i_g = C \frac{\Delta x}{x} \cdot \frac{U}{\sqrt{x}} \cdot \frac{\eta}{n\sqrt{\kappa}(1+\eta)^2} \quad (8)$$

From this we find one condition for maximum deflection by differentiating (8) with respect to η and equating to zero. As a result we obtain $\eta = 1$. In order to increase the sensitivity we should now try to make n and k as small as possible. In this respect we are limited to the condition $n > 1$, as otherwise R_u would be negative — an

impossibility. By reducing κ without changing the other constants we reduce the current sensitivity and we have to show how far this is permissible.

We have not yet introduced the condition

$$R_u = R_c - g = g(n - 1) \quad (9)$$

Near balance we find:

$$R_u = X \frac{\eta(1 + \lambda)}{1 + \eta}$$

and this gives us

$$\frac{\eta(1 + \lambda)}{1 + \eta} = \kappa(n - 1) \quad (10)$$

For $\eta = 1$ we obtain:

$$1 + \lambda - 2\kappa(n - 1) = 0 \quad (11)$$

and for $\Delta\alpha$ we have found with $\eta = 1$:

$$\Delta\alpha = C \frac{\Delta x}{x} \frac{U}{\sqrt{x}} \frac{1}{4n\sqrt{\kappa}}$$

We are now seeking the minimum of $n\sqrt{\kappa}$ with the subsidiary condition (11).

According to the procedure of Lagrange we write:

$$n\sqrt{\kappa} + 2\kappa\psi(n - 1) - (1 + \lambda)\psi = \Phi(n, \kappa, \psi) \quad (12)$$

where ψ is a constant of proportionality.

From (12) we find by differentiating once in respect to n and then to κ the optimum values of n and κ :

$$\frac{n}{2\sqrt{\kappa}} + 2\psi(n - 1) = 0 \quad (13a)$$

$$\sqrt{\kappa} + 2\psi\kappa = 0 \quad (13b)$$

and these equations together with (11) give us:

$$n = 2; \kappa = \frac{\lambda + 1}{2}$$

With these values we obtain

$$\Delta\alpha = C \frac{\Delta x}{x} \frac{U}{\sqrt{\kappa}} \frac{1}{8\sqrt{(\lambda + 1)/2}} \quad (14)$$

or

$$\begin{aligned} R_c &= 2g & g_{\min} &\rightarrow \frac{x}{2} \\ a_{\min} &\rightarrow 0 \end{aligned}$$

The last value is limited by the permissible heat dissipation.

The solution therefore gives three conditions:

- a) The ratio r/x should be unity.
- b) The galvanometer resistance should be equal to the resistance of the outer circuit.
- c) The galvanometer should be positioned between the junction of the high resistance bridge arms and the junction of the low resistance bridge arms.

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ENCOUNTER OF VEHICLES AT INTERSECTIONS

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1. The crossing of a road junction or intersection by a vehicle involves two main kinds of danger:

- a) the danger of sideways skid or overturning along the vehicle's curved path;
- b) the danger of collision at points of intersection of two or more vehicle paths.

In the latter case, the probability of collision depends on the traffic intensity and the number of points of intersection.

2. In Figure 1, l denotes the length of the vehicle, b its width, L the distance between two vehicles driving in single file, v their speed, and D the width of the intersection. For the sake of simplicity, it is assumed that the above quantities are constant and equal in all directions. We then have:

For a vehicle in lane I, the time required for traversing the intersection is $\frac{D + l}{v}$, and the time interval between successive arrivals of vehicles at the intersection is $\frac{L + l}{v}$.

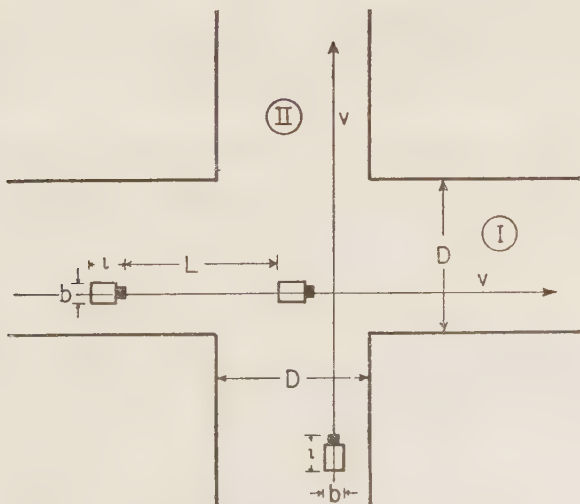


Figure 1

Hence, the time fraction during which the intersection is occupied by vehicles in lane I is $p = \frac{D+l}{v} / \frac{L+l}{v} = \frac{D+l}{L+l}$; the time fraction during which lane II is occupied by vehicles in lane I is $p' = \frac{b+l}{L+l}$, and this is also the probability of lane II being occupied by a vehicle (or part of a vehicle) in lane I at a random moment.

Similarly, the time fraction during which lane I is occupied by vehicles in lane II is $p'' = \frac{b+l_s}{L+l}$.

For unregulated traffic, flowing independently in both lanes, the probability of encounter of two vehicles at the intersection of lanes I and II is

$$P = p' p'' = \left(\frac{b+l_s}{L+l} \right)^2 \quad (1)^*$$

3. It is known that for vehicles driving in single file a minimum "safe distance", $L = tv + cv^2$ (t = reaction time of driver; c = braking coefficient) is prescribed. Assuming that the "safe distance" rule is adhered to, substituting the above value for L gives

$$P = \left(\frac{b+l}{l + tv + cv^2} \right)^2 \quad (2)^{**}$$

It is assumed that L is larger than b ; otherwise we shall have the case of traffic flow in one direction only.

From Eq. (2) it can be seen that as the speed approaches zero the probability of encounter becomes very high. The speed corresponding to the minimum encounter probability can be determined by equating P to zero; then $l + tv + cv^2 = \infty$, or $v = \infty$.

* In the case of different vehicle dimensions and spacing for each lane, the respective time fractions would be $p' = \frac{b'' + l'}{L' + l'}$ and $p'' = \frac{b' + l''}{L'' + l''}$, and the probability of encounter

$$P = \frac{b'' + l'}{L' + l'} \times \frac{b' + l''}{L'' + l''}$$

** In the general case of a traffic intensity of n vehicles per hour at a given speed, the time interval between the arrivals of successive vehicles at the intersection is $3600/n$, the time fraction during which lane II is occupied by vehicles in lane I is $\frac{(b+l)n}{3600v}$ and the probability of encounter

$$P = \left[\frac{(b+l)n}{3600v} \right]^2 \quad (3)$$

Eq. (2) is, in fact, the special case of a road carrying traffic at a capacity

$$n = N = \frac{3600v}{l + tv + cv^2}$$

The conclusion is that the higher the speed, the smaller the probability of encounter. It should be borne in mind, however, that the probability of encounter is only one aspect of the risk involved in crossing the intersection. Another factor to be taken into consideration is the amount of possible damage in a collision, which may be assumed as proportional to the kinetic energy of the colliding vehicles, i.e. to the square of their speed (assuming the mass equal to 2). This enables us to define a *damage function* $R = Pv^2$, or

$$R = \left(\frac{b + l}{l + tv + cv^2} \right)^2 v^2 \tag{4}$$

which can serve as a measure of the risk involved in a collision at full traffic capacity.

In order to analyse the properties of R as a function of the speed, we equate its first derivative to zero

$$R' = \frac{(b + l) v (cv^2 - 1)}{(l + tv + cv^2)^3} = 0,$$

the alternatives being (a) $v = 0$ or $R = 0$, (b) $v = \infty$ or likewise $R = 0$, and

$$(c) \ v = \sqrt{\frac{l}{c}} \text{ or } R_{\max} = \left[\frac{(b + l) \sqrt{\frac{l}{c}}}{2l + t \sqrt{\frac{l}{c}}} \right]^2.$$

The value $v = \sqrt{l/c}$ is the optimum speed corresponding to the maximum traffic capacity of the road³; it is interesting to note that it also corresponds to the maximum value of the “damage function”, as shown here.

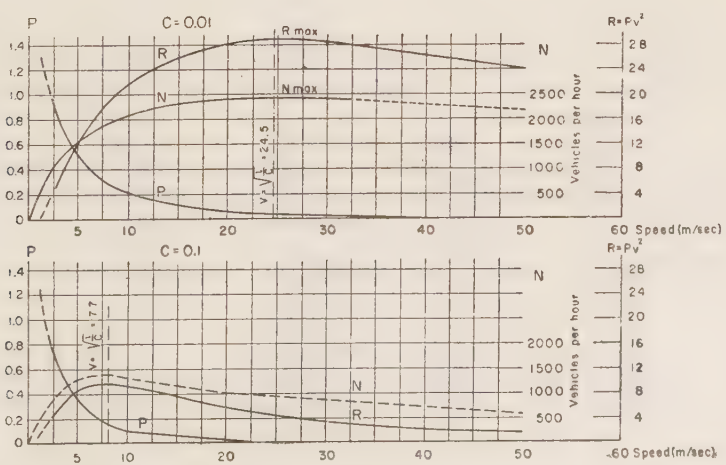


Figure 2

Substituting numerical values: $b = 2.0$ m, $l = 6.0$ m, $t = 1.0$ sec, $c = 0.01$ sec²/m. we obtain $v = 24.5$ m/sec, $R = 28.8$ m²/sec², whereas for $c = 0.1$ sec²/m we would have $v = 7.7$ m/sec, $R = 9.8$ m²/sec².

Values of P , N and R for $c = 0.01$ and $c = 0.1$ respectively, at different speeds, are given in Table I below, based on the same dimensional data. The diagrams in Figure 2 show that for speeds below $\sqrt{l/c}$ the probability of encounter increases, but the damage function tends towards zero. For speeds above $\sqrt{l/c}$, however, the probability of encounter tends towards zero, while the damage function remains almost constant over a wide range of speeds, and only starts decreasing slowly again at high speeds.

TABLE I

	Speed v (m/sec) (km/h)	Traffic capacity N (vehicles per hour)	Probability of encounter P	Damage function R (m ² /sec ²)	Collision index K
$c = 0.01$					
1	3.6	502	(1.31)	(1.31)	(21.00)
2	7.2	990	0.99	3.96	15.84
3	10.8	1185	0.78	7.02	12.45
4	14.4	1408	0.62	9.92	9.93
5	18.0	1600	0.51	12.75	8.16
6	21.6	1746	0.42	15.12	6.72
8	28.8	1968	0.30	19.20	4.80
10	36.0	2120	0.22	22.00	3.52
20	72.0	2400	0.071	28.40	1.13
30	108.0	2400	0.032	28.80	0.51
40	144.0	2324	0.0167	26.80	0.27
50	180.0	2225	0.0097	24.40	0.15
$c = 0.1$					
1	3.6	506	(1.27)	(1.27)	(20.30)
2	7.2	857	0.91	3.64	14.55
3	10.8	1090	0.65	5.85	10.39
4	14.4	1238	0.48	7.70	7.67
5	18.0	1332	0.35	8.75	5.60
6	21.6	1384	0.26	9.34	4.16
8	28.8	1410	0.15	9.62	2.40
10	36.0	1385	0.095	9.50	1.52
20	72.0	1092	0.0147	5.88	0.235
30	108.0	860	0.00403	3.62	0.064
40	144.0	756	0.00151	2.42	0.024
50	180.0	588	0.000685	1.71	0.011

Dimensional data: $b = 2.0$ m; $l = 6.0$ m; $t = 1.0$ sec; $m = 2$; $S = 16$.

4. The total probable number of encounters, which can also be referred to as the collision index, is $K = SP$, where S is the number of points of path intersection, or, substituting the value of P for the general case (Eq. 3)

$$K = S \frac{(b+1) n^2}{3600v} \quad (5)$$

The collision indices calculated with the aid of this formula for an intersection of four two-lane roads* ($S = 16$) are also given in Table I. In practice, the number of collisions that take place at an intersection is much less than that given in Table I; the reason being, of course, the intervention of human control—whether in the form of traffic signals at regulated intersections, or of the drivers' precautions in attempting to avoid collision at unregulated intersections. These indices should therefore rather serve as a guide for the comparative evaluation of the degree of traffic disorder and damage capacity of unregulated intersections, and as a criterion of the degree of regulation required.

5. The maximum permissible collision index for a given intersection, i.e. the limit above which traffic regulation is called for, is determined on the basis of collision statistics and depends on a variety of factors, such as the individual qualities of the drivers, the general condition of the vehicles, etc. For example, for an intersection carrying 100 vehicles per hour (dimensional data as above) at a speed of $v = 5$ m/sec (18 km/h), the collision index would be

$$K = 16 \times \left[\frac{100(2+6)}{360 \times 5} \right]^2 = 0.032.$$

Considering that only a small fraction of the encounters actually develop into collisions, it appears reasonable to assume $K = 0.02$ as the maximum permissible collision index.

The maximum permissible collision index determines the corresponding values of the probability P and the damage function R . In addition, it is desirable to define a limit for the product $Pmv^2/2$, since it is obvious that for a given speed, the heavier the vehicles involved, the lower is the permissible collision index called for.

ACKNOWLEDGMENT

The author is indebted to Dr. P. Naor for valuable advice and comment.

* The term "road" refers here to the approach beginning at the centre of the intersection.

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LETTER TO THE EDITOR

Shear stresses in a square diamond section, A. ZASLAVSKY, Technion — Israel Institute of Technology, Haifa.

Literature on strength of materials does not usually deal with shear stresses in a square section subjected to the action of a shear force S along the *diagonal*. In the few cases where the subject is treated^{1,2,3}, the vertical shear stresses τ_{zy} are calculated by the usual shear formula which

$$\tau_{zy} = \frac{SQ}{Ib} \quad (1)$$

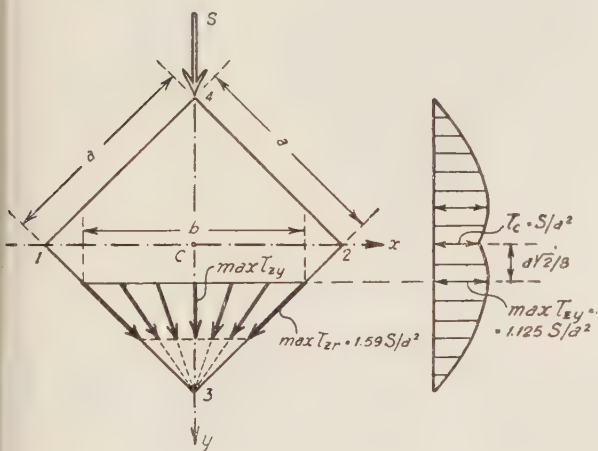


Figure 1

(b)

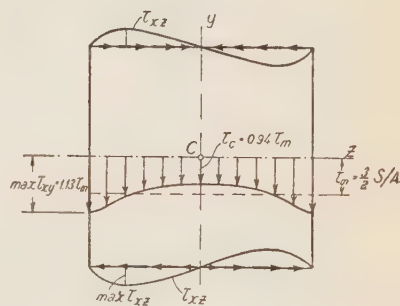


Figure 2

is based on the assumption that the stresses τ_{zy} are uniformly distributed over the (variable) width b (Figure 1). Furthermore, the assumption is made that the resultant shear stresses τ_{xz} are directed towards the upper and lower corners respectively. Stresses thus calculated are given in Figure 1a, and 1b, and the distribution of τ_{zy} along the diagonal y in Figure 1b.

Assuming that uniform stress distribution holds in the case of a shear force acting *parallel* to the sides of the section (the rigorous solution shows that this is not true even in this case, see Figure 2), it will be shown that the above assumptions are not justified and that the stress distribution is according to Figure 4.

Resolving S into two components $S_{x'} = S_{y'} = S/\sqrt{2}$ (Figure 3) we have by (1) for any point $P(x, y) = P(x', y')$:

$$\left. \begin{aligned} \tau_{zx'} &= \frac{6}{\sqrt{2}} \frac{S}{a^4} \left(\frac{a^2}{4} - x'^2 \right) \\ \tau_{zy'} &= \frac{6}{\sqrt{2}} \frac{S}{a^4} \left(\frac{a^2}{4} - y'^2 \right) \end{aligned} \right\} \quad (2)$$

The resultant shearing stress τ_{zy} is thus:

$$\tau_{zy} = \sqrt{\tau_{zx'}^2 + \tau_{zy'}^2} \quad (3)$$

and its direction:

$$\operatorname{tg} \alpha = \frac{\tau_{zy'}}{\tau_{zx'}} = \frac{(a/2 - y')(a/2 + y')}{(a/2 - x')(a/2 + x')} = \operatorname{tg} \beta \operatorname{tg} \gamma \quad (4)$$

β denotes the direction towards the corresponding corner 3, and γ — towards the opposite corner 4.

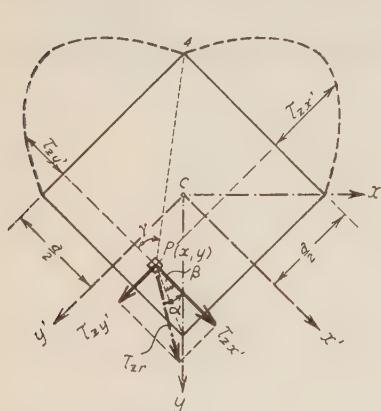


Figure 3

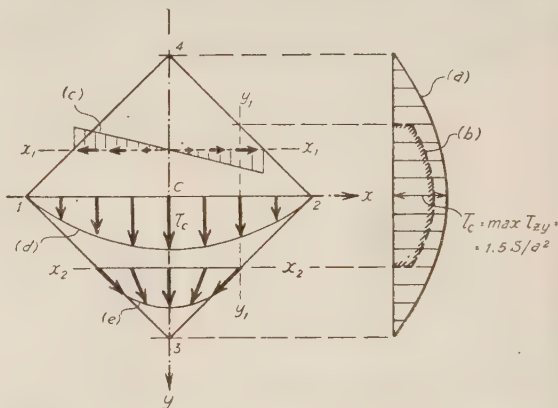


Figure 4

Thus it is seen that the resultant stress is directed towards the corners only for points lying on the vertical diagonal y or on the periphery. Resolving the resultant stress in the directions x and y we obtain the vertical and horizontal shear components acting in the plane of the section:

$$\left. \begin{aligned} \tau_{zx} &= -\frac{6S}{a^4} xy \\ \tau_{zy} &= \frac{3S}{a^4} \left[\frac{a^2}{2} - (x^2 + y^2) \right] \end{aligned} \right\} \quad (5)$$

The parabolic variation of τ_{zy} along the vertical diagonal y and the vertical line $y_1 - y_1$ is shown in Figure 4, a and b respectively. The linear variation of τ_{zy} over the width $x_1 - x_1$ is shown in Figure 4, c. The distribution of τ_{zy} over the horizontal diagonal x and the width $x_2 - x_2$ is shown in Figure 4, d and e respectively. At the corners 1, 2, of course, $\tau_{zy} = 0$, as it should be (contrary to Figure 1).

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EFFECT OF ALKALINE MEDIA UPON CORROSION OF MILD STEEL UNDER VARIOUS CONDITIONS

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ABSTRACT

Tests were carried out on submerged mild steel specimens in hydroxide solutions and cement mortar extracts, both in the presence and absence of salts and under varying degrees of aeration, with a view to determining the pH required for inhibiting corrosion of reinforcing steel in concrete. The quantity of rust was determined by the weight loss method at one month and three months.

It was established that in $Ca(OH)_2$ solutions, in the absence of salts, corrosion decreases gradually with increasing pH until inhibition sets in. In the presence of salts no gradual effect was observed, but inhibition could be obtained at high pH . The pH level required for inhibition increases with the degree of aeration both in the presence and absence of salts. When the "complete inhibition level", a constant value for each medium, is reached, aeration ceases to have effect.

Small quantities of salts intensify corrosion while very high concentrations have a restraining effect.

INTRODUCTION

Reinforced concrete has assumed ever-increasing importance in engineering construction. Countless reinforced concrete structures have been built all over the world, and in Israel practically all structural members in building are made of reinforced concrete. Hence, the durability of this material has become a matter of concern to both practical engineers and researchers.

As is well known, concrete is strong in compression, but relatively weak in tension. In structural components made of concrete, tensile resistance, and sometimes added resistance to compression, is provided by steel bars embedded in the concrete.

Reinforced concrete of average quality is a very durable material, owing to the inherent durability of concrete and to the protection against corrosion afforded to the steel by the concrete covering it.

This protection is due to the alkalinity of concrete, resulting from the presence of free calcium hydroxide produced from the cement by hydrolysis by water. In general, increasing alkalinity within the limits found in concrete reduces the rate of corrosion because of reduction both of the e.m.f. of the Fe/H_2 half-cell and of the solubility of $Fe(OH)_2$, the reduced solubility permitting the formation of a protective layer over the steel.

The binding material in concrete, usually Portland cement, is composed mainly of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$ (the silicates amounting to some 75%), $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. By hydrolysis of the silicates by the water added at the time of making concrete, calcium hydroxide is formed, as for example:



In addition to the Ca(OH)_2 , the alkalis present in cement (usually about 1%) add to the alkalinity of concrete.

In spite of the inhibitory property of concrete, however, many cases of severe corrosion of reinforcement have been observed. Corrosion products, occupying a volume much greater than that of the iron from which they are formed, eventually lead to flaking off and cracking of the concrete overlying the steel. Corrosion is a result either of poor quality of the concrete or of severe conditions of service, the most common causes being the action of sea salts (in maritime structures) and carbonation of the concrete.

Not enough has hitherto been known about the hydroxyl ion concentration required for inhibition under the various conditions, such as aeration, presence of salts, etc.

Preliminary tests indicating that the behaviour of steel in concrete is analogous to that in aqueous solutions, a study of submerged corrosion of steel in alkaline media of varying hydroxyl ion concentration was undertaken with the object of acquiring more knowledge about the factors controlling inhibition of corrosion of reinforcing steel.

EXPERIMENTAL

Characteristics of the media varying in composition and hydrogen ion concentration, and of the steel, are given in Tables I and II.

TABLE I
Characteristics of media

Salt-free media		Salt-containing media	
Composition	pH at 25°C	Composition	pH at 25°C
Boiled distilled water	7.0	Distilled water + 3.5% NaCl	6.6
Tap water	7.1	Mediterranean Sea water	7.9
NaOH solution	12.7	Ca(OH)_2 + NaCl	10—12.6
Ca(OH)_2 solutions	10—12.6	NaOH + NaCl	10—14.0
Cement mortar extracts	11.8—12.2	Cement mortar made with sea water and extracted with sea water	10—12.5
		Cement extract (with sea water)	12.8

TABLE II
Chemical analysis of the steel, tap water and sea water

Steel		Tap water		Sea water	
	%		<i>p.p.m.</i>		<i>g/l</i>
C	0.1	Chlorides (calc. as NaCl)	250	NaCl	27.200
P	0.05	Total solids	670	K ₂ SO ₄	0.863
S	0.07	Total hardness	450	MgCl ₂	3.810
Mn	0.4	Alkalinity (as bicarbonate)	350	MgSO ₄	1.660
Cu	0.04	Conductivity	1300 micromho	CaSO ₄	1.260
				MgBr ₂	0.076
				Total	35.732

Pickled mild steel bars, 6 mm in diameter and 80 mm in length, were used for the tests. The pickling solution consisted of 10% hydrochloric acid and an inhibitor (dinitrophenylthiobenzothiazol 'URCA') which afforded practically complete protection to the uncorroded steel. The 'coefficient of inhibitor failure' was determined and taken into account where necessary. The cleansed and weighed bars were put into glass containers filled with the various solutions for a period of up to 3 months, during which the development of corrosion, its distribution and character were observed. The time effect was studied for 480 days. At the end of the tests, the bars were cleansed as above, re-weighed and the quantity of rust determined.

Parallel specimens of unpickled bars were also tested.

TEST RESULTS

A. Steel bars immersed in solutions in open glass containers

The following observations relate to steel bars immersed in solutions in open glass containers. The volume of the solution was kept constant by addition of distilled water, whenever necessary. The *pH* values given are the initial ones.

Corrosion started at the ends of the bars, the area in contact with glass being particularly affected, and developed rapidly all over the bars in solutions of low *pH*, becoming progressively localised with increase of the *pH*. The hydroxyl ion concentration affected also the shape of the corrosion products and their colour. In solutions of low *pH* a voluminous precipitate consisting of a gelatinous mixture of hydrated iron oxides was produced. The bars were covered with large loose flakes which, however, were conspicuous by their absence on the end sections. In solutions of higher *pH*, the localised rust appearing here and there formed flower-like tubercles, sometimes quite compact. In solutions of high *pH* only a change in the colour of the bars was observed.

The first corrosion products noticeable were green ferrous hydroxide, which oxidised to the less soluble hydrated oxides, so that the rust was stratified, brown outside, green or black underneath. The localised rust was particularly dark, almost black. The rate of change and the final colour depended on the composition of the solutions and degree of aeration.

1. *Boiled distilled water, pH 7.0*

Loose flakes covered the steel bars immediately upon immersion (see Figure 1). The quantity of rust determined at 3 months was 1.54% of the bar weight.

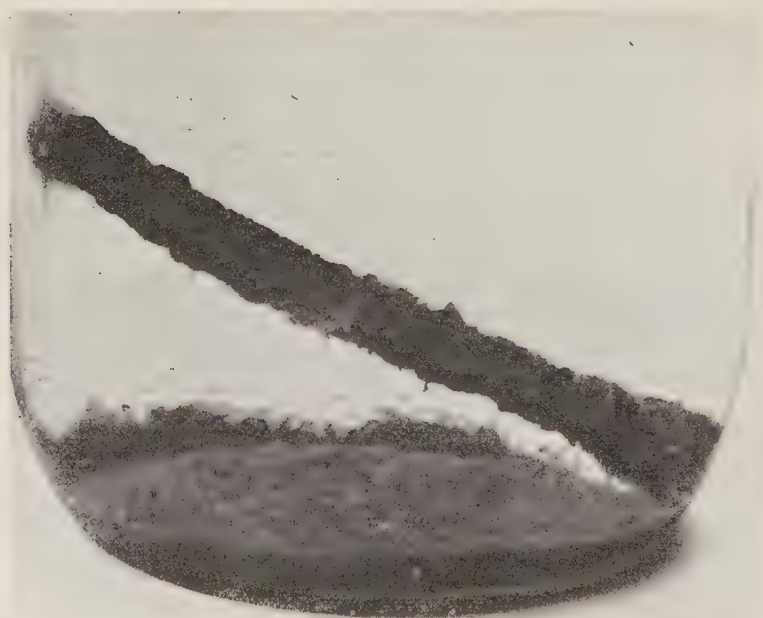


Figure 1

Rust on steel bar stored for 3 months in distilled water.

2. *Tap water, pH 7-8*

The character of the rust was similar to that in distilled water, but the quantity only 0.65% of the bar weight. The end sections were dotted with miniature holes, revealed after cleansing of the bars.

3. *NaOH solution, pH 12.7*

The bars remained clean except for one of the end sections, which initially became green and later changed to brownish. After cleansing pinholes were revealed and a weight loss of 0.14% was found.

4. Ca(OH)_2 solutions, pH 12.3–12.5

Dark brown stains covered the end sections, while the rest of the bar only lost its shine. The quantity of rust was about 0.1% of the bar weight.

5. Cement mortar extracts in tap water, pH 11.8–12.1

In the extract of pH 11.8 loose brown flakes covered the bars almost entirely, while at pH 12.1 they remained practically clean. In both cases the end sections were pinholed.

B. Effect of pH and of aeration

To find the effect of pH and of aeration, parallel specimens were immersed in glass containers filled with Ca(OH)_2 solutions of pH 10–12.65. One half of the glass containers were closed with a screwed lid so that very little air penetrated, while others were subjected to intensive aeration with CO_2 -free air. The results are given in Table III.

TABLE III
Effect of the pH of Ca(OH)_2 solution and of aeration

pH	10.0	10.5	11.0	11.5	12.0	12.65
Ca(OH)_2 (g/l)	0.004	0.012	0.037	0.117	0.370	1.655
Rust in aerated solution (% of bar weight)	2.46	2.20	2.00	1.80	0.02	0.01
Rust in non-aerated solution (% of bar weight)	0.74	0.81	0.30	0.10	0.02	0.02

The data in Table III show that the higher the pH value, the less the rust both in aerated and non-aerated solutions, until a level of practically complete inhibition is reached. They also show that aeration affects corrosion very considerably up to a certain pH level. Under test conditions this level was pH 12.

C. Effect of salts

As is well known, the presence of salts, particularly of chlorides in solution, intensifies corrosion of steel¹. The first product to form is soluble ferrous chloride and the hydroxide is produced in a secondary reaction when the ferrous salt encounters hydroxyl ions. For the formation of a protective layer in direct contact with the steel a fairly high concentration of hydroxyl ions is required. Even then the protective properties of this layer are adversely affected by the salts.

To study the effect of salts on corrosion, their influence on the pH values was determined in solutions containing an excess of solid Ca(OH)_2 , similar to that found in concrete and mortars.

1. Effect of salts on the pH value of solutions

The effect of NaCl, sea salt and CaCl_2 on a saturated Ca(OH)_2 solution with an excess of solid hydroxide* is shown in Figure 2. Concentrations ranged from 0 to 300 g/l.

It should be noted that the salts affect the pH both by increasing the solubility of Ca(OH)_2 and by decreasing the pH of the solution.** The effect measured is the

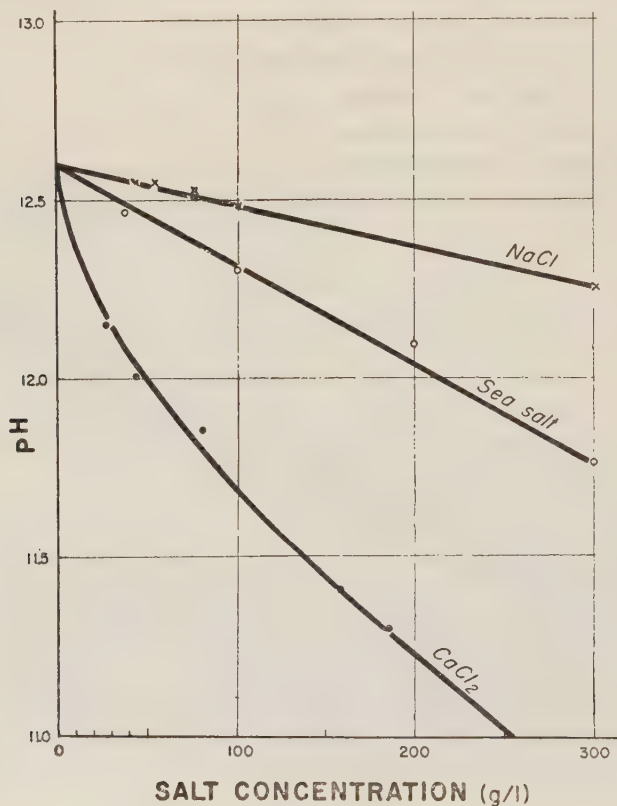


Figure 2
Effect of salts upon the pH of saturated Ca(OH)_2 solutions

outcome of both actions. Thus, in the absence of an excess of solid calcium hydroxide, the reduction of the pH by chlorides is higher. It has been found that the order of magnitude of the difference is 0.2. From the data in Figure 2 it can be assumed that pH reduction is nearly directly proportional to the salt concentration.

* Precautions were taken to prevent carbonation.

** Possible errors in the determination of the pH values, due to the presence of sodium ions, were neglected, as a lithium-glass electrode was used.

The effect of salt concentration on the pH of unsaturated $Ca(OH)_2$ solutions was found to be very similar to the above (see Figure 3).

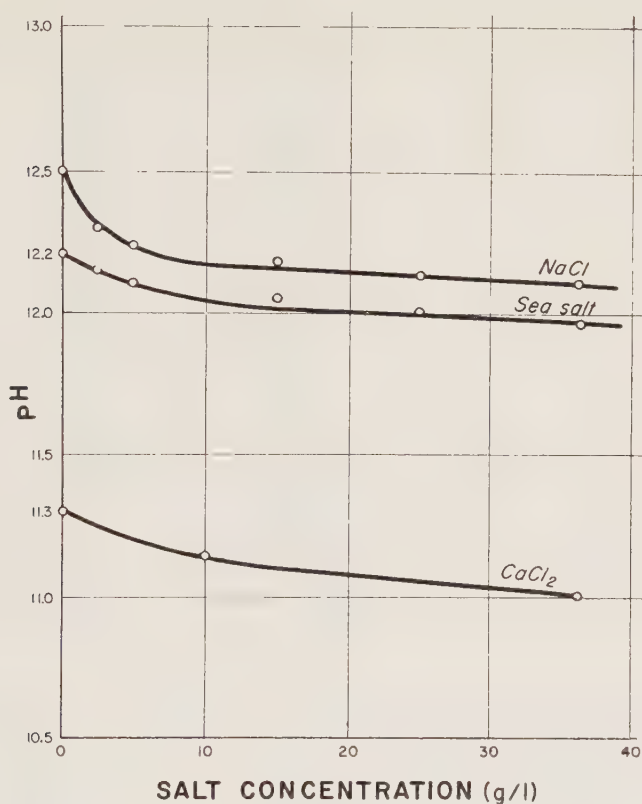


Figure 3
Effect of NaCl upon the pH of $Ca(OH)_2$ solutions
(Initial pH 11.3, 12.2, 12.5 respectively).

2. Effect of salts on rust development

In distilled water containing 35 g/l NaCl, with pH 6.6, green corrosion stains showed immediately, taking later the form of brownish flakes covering the bars entirely. The quantity of rust was 1.36% of the bar weight.

In Mediterranean Sea water with pH 7.9 the phenomenon was similar to that in distilled water with sodium chloride, the difference being in the smaller size and greater compactness of the flakes. The quantity of rust was about 0.9% of the bar weight.

The effect of the pH value and aeration of various alkaline solutions containing salts is shown in Table IV.

Figure 4 →

Pits on bars after removal of localised corrosion products



Figure 5 ↓

Rust on bars stored in concrete extracts of varying pH



Bars immersed in a sea-water extract of concrete were covered with large flakes all over at pH 10. At higher pH the flakes became smaller and covered only parts of the bars. Finally, at pH 12 the rust became extremely localised, consistent with the known action of anodic inhibitors present in a quantity nearly, but not quite, sufficient for complete inhibition. The corrosion products, in the form of very dark, voluminous tubercles, concentrated mainly at the ends of the bars, the areas of contact with glass being particularly affected. In Figure 4 characteristic deep pits revealed after removal of corrosion products are shown. The end sections of the bars were densely dotted with small holes, giving the appearance of a fine sponge.

At still higher pH (12.75) the bars remained free of rust, except for a fine greenish film (see Figure 5).

At a pH level close to complete inhibition, there was a marked difference between the behaviour of steel bars immersed in salt-free and salt-containing solutions.

TABLE IV

*Effect of pH and of aeration in the presence of salts
Quantity of rust (% of bar weight) at 3 months*

Initial pH value	Concrete extract*		Ca(OH) ₂ + 36 g/l NaCl		NaOH + 36 g/l NaCl	
	Limited air access	Aerated	Limited air access	Aerated	Limited air access	Aerated
10.0	0.63	0.95	0.63	1.58	0.80	2.36
10.5	—	1.20	0.78	1.50	—	—
11.0	0.50	1.10	0.70	1.46	0.50	2.00
11.5	0.56	0.70	0.86	1.52		
12.0	0.65	0.85		1.41	0.45	1.86
12.45	0.40	0.50				
12.60			0.07	1.08		
12.75**	0.04	0.02				
13.0					0.05	0.50
14.0					0	0

* Made with sea water and extracted with sea water.

** Portland cement extract in sea water.

In the former case the localised corrosion resulted in peeling off of thin layers, while in the latter pronounced pitting, often very deep, was observed.

D. Effect of aeration

One series was devoted to the study of the effect of different degrees of aeration. The results are presented in Table V.

TABLE V
Effect of aeration

Solution	pH	Quantity of rust at one month (% of bar weight)
Sea water concrete extract, oxygen-free*, hermetically closed	10.3	0.01**
Ca(OH) ₂ + 36 g/l NaCl, hermetically closed	12.2	0.04
Ca(OH) ₂ + 36 g/l NaCl, non-hermetically closed	12.2	0.35
Ca(OH) ₂ + 36 g/l NaCl, aerated with CO ₂ -free air	12.2	0.50

* Solution deoxygenated with iron. ** At 3 months.

E. Effect of sodium chloride concentration

As is known, salt concentration affects corrosion. In addition to the effect of the salt, its presence increases the conductivity of the solution and reduces the solubility of oxygen. As the salt content in the solution becomes higher, the increase of the conductivity of the solution ceases, while the solubility of the oxygen keeps diminishing until at a certain concentration the shortage of oxygen has a predominant effect.

To find the final effect, submerged corrosion in Ca(OH)₂ solutions containing various quantities of sodium chloride was studied. Results are given in Tables VI, VII, VIII.

TABLE VI
Sodium chloride effect on rust development in Ca(OH)₂ solutions of different pH in hermetically closed containers

NaCl (g/l)	pH	Quantity of rust (% of bar weight)
Tests at 1 month		
0	12.4	
1	12.3	0.01
20	12.1	0.02
30	12.0	0.04
50	11.9	0.05
Tests at 3 months		
0	12.50	0
2.5	12.30	0
5	12.25	0.02
15	12.20	0.06
25	12.15	0.06
35	12.10	0.11

TABLE VII

Effect of sodium chloride in Ca(OH)_2 solutions of different pH with limited air access

NaCl (g/l)	pH	Quantity of rust at 1 month (% of bar weight)	NaCl (g/l)	pH	Quantity of rust at 3 months (% of bar weight)
0	11.3	0.35	0	12.68	0
10	11.15	0.57	35	12.6	0.04
35	11.0	0.60	45	12.55	0.18
100	10.9	0.14	55	12.55	0.07
300	10.7	0.11	75	12.5	0.05

TABLE VIII

Effect of sodium chloride in Ca(OH)_2 solutions with limited air access (CO_2 -free air)

NaCl (g/l)	pH	Quantity of rust at 1 month (% of bar weight)
1	12.5	0.01
20	12.35	0.04
50	12.25	0.03
100	12.15	0.03
300	11.45	0.01

A schematic representation of the effect of salt concentration is given in Figure 6.

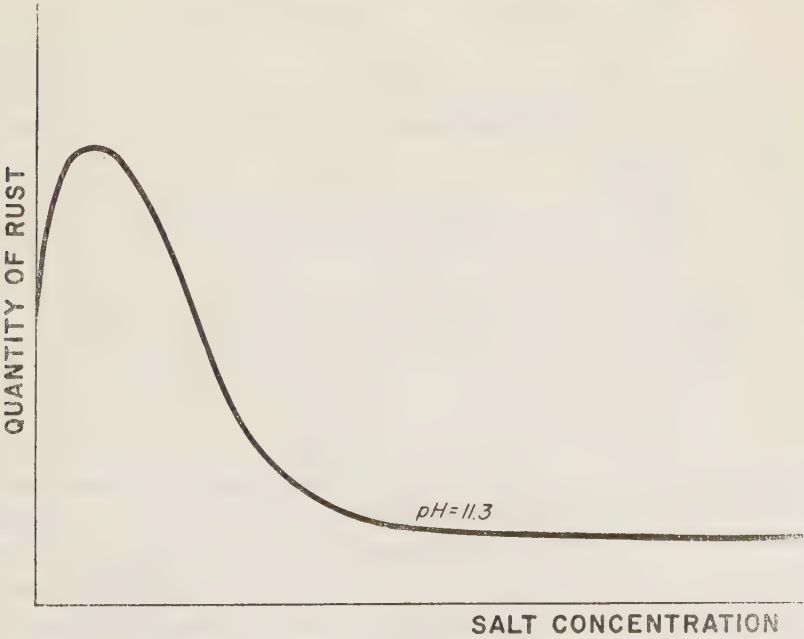


Figure 6

Schematic representation of the effect of salt concentration on rust development in Ca(OH)_2 solutions

F. Effect of time

Steel bars were immersed in sea water extracts of concrete made with sea water. The pH values of the extracts ranged from 9.5 to 12.65. The bars were tested for rust up to 480 days. A schematic representation of the results is given in Figure 7.

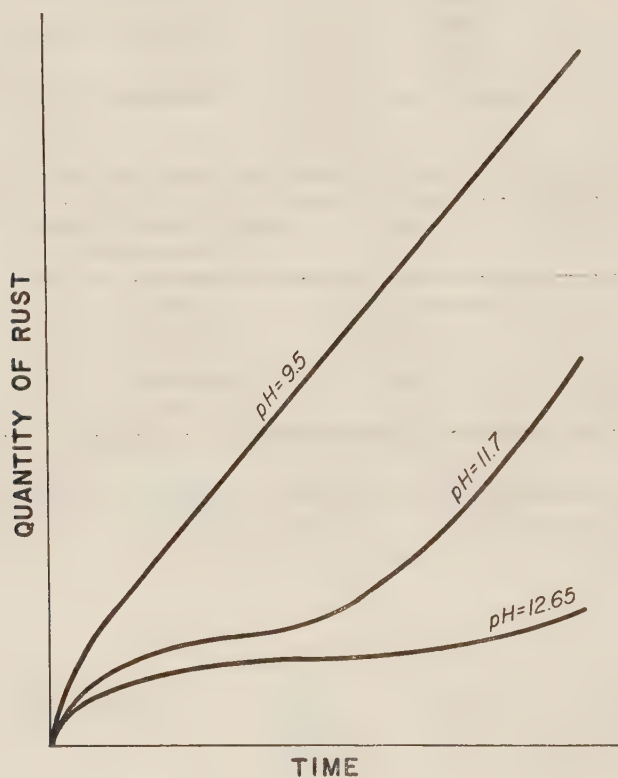


Figure 7

Schematic representation of the rate of corrosion at different pH levels

G. Effect of temperature

To find the effect of temperature on submerged corrosion in sodium hydroxide solutions of different pH, with and without salt, tests were made on bars immersed in full, hermetically closed containers with only dissolved oxygen available for reactions. The temperatures were 25°C, 35°C and 50°C, the last, unfortunately, not maintained owing to faulty functioning of the thermostat; it is possible that the fluctuation in temperature, though small, have affected the quantity of rust measured. Results are given in Table IX.

TABLE IX
Effect of temperature

pH	Quantity of rust at 5 months (% of bar weight)						
	Temperature	25°C		35°C		50°C	
	NaCl (g/l)	0	36	0	36	0	36
9.9		0.02	0.02	0.03	0.03	0.58	2.17
10.9		0.02	—	0.02	—	0.97	—
11.8		0	0.01	0	0.01	0	2.32
13.1		—	0	—	—	—	0.01

H. Behaviour of unpickled bars

Parallel tests with unpickled steel bars have not shown any significant difference in behaviour compared with the pickled specimens, except that the end sections of the former were more vulnerable to corrosion.

DISCUSSION

The authors have been engaged for a number of years in studying the behaviour of reinforcement embedded in mortar and concrete. Results obtained so far were summed up in two papers^{2,3}. They indicated, as could be expected, a pronounced similarity between the behaviour of reinforcing steel in concrete and that of steel bars immersed in aqueous alkaline solutions. Now, the use of solutions simplifies the study of corrosion by eliminating the complications due to the intrinsic heterogeneity of concrete and the differential conditions usually prevailing. Accordingly, alkaline solutions with pH values within the range found in concrete were used, and variations in temperature and aeration, similar to those prevailing in reinforced concrete structures in practice, were allowed.

The experiments showed that in the absence of salt the quantity of rust depends directly upon the alkalinity, and within the range of the tests, the higher the pH of the solution, the less the rust (see Table III). Close to the pH level affording complete inhibition, the corrosion, though localised, did not show pitting, in contrast to concrete where pitting may occur due to the differential conditions in the layer overlying the steel².

The problem of the effect of salts on corrosion of reinforcement arises in maritime reinforced structures either through direct contact with sea water or through penetra-

tion of airborne salts, as well as in concretes mixed with sea water (permitted by Codes and standard specifications in certain countries). Calcium chloride is also often added in cold-weather concreting.

In the presence of salts, the effect of increasing alkalinity, up to a certain pH value, is practically non-existent, although the effect on the character of the rust remains pronounced.

Under limited aeration, corrosion increases with salt concentration, reaching a maximum at 20–50 g/l of sodium chloride, the exact value depending on test conditions (see Tables VII and VIII). Small quantities of salts intensify corrosion, while very high concentrations have a restraining effect (Figure 6) owing to shortage of oxygen (see p. 73–75 and ref. 5).

In hermetically closed containers filled with calcium hydroxide solutions of pH 12.2–12.5, a steady increase in rust was measured up to 50 g/l NaCl (see Table VI).

The above data apply only to the test conditions under consideration; under a different set of conditions a different relationship may evolve. Hence, it is not suggested that these data permit general quantitative deduction, but rather that they give an indication of trends. Considering the well-known difficulties in corrosion tests due to the interrelationship of the various factors involved, only large numbers of data would supply quantitative information.

Results presented in Tables III, IV and V show that both in the absence and presence of salts the rate of corrosion increases with the intensity of aeration. Thus, the pH required for inhibition also depends upon the degree of aeration. By increasing the hydroxyl ion concentration, however, a level may be reached at which aeration has practically no effect. It is suggested that this level (dependent only on the composition of the solution) be called 'complete inhibition level'; Tables III and IV show that it is higher in the presence of chlorides than in their absence.

In the case of limited air access, complete protection of the steel can be obtained by a lower hydroxyl ion concentration. The corresponding pH value, called by the authors 'inhibition level', depends both on the composition of the solution and the degree of aeration. The results show that in a NaOH + 36 g/l NaCl solution the 'complete inhibition level' was pH 14.0, while the 'inhibition level' was pH 13.0. In the presence of salts, a saturated calcium hydroxide solution of pH 12.6 almost reaches the inhibition level (little localised corrosion after 3 months), while a complete inhibition level is unattainable.

Concrete, as already mentioned, would always permit some penetration of air⁶. A dense concrete can be assumed to allow very limited air access; thus an 'inhibition level' is sufficient. This level is readily afforded by concrete in the absence of salts² but not in their presence, since while their presence necessitates a higher alkalinity, the salt reduces the pH . In concrete, this reduction is even greater than in the corresponding solutions*.

* In addition, "cell concentration" corrosion develops.

In a porous concrete, where aeration is intensive, a complete inhibition level is required. In the absence of salts, fresh concrete has a sufficient pH^3 but porosity permitting deep carbonation leads to a reduced pH and is likely to leave the steel in an environment favourable to corrosion. Should sea salt penetrate into such a concrete, the reinforcement could become highly vulnerable to corrosion.

On the other hand it has been found³ that the pH values of concrete permanently immersed in water (with or without salts) are high enough (12.95) to afford complete inhibition.

CONCLUSIONS

The observations and data obtained lead to the following conclusions:

1. The pH value required for inhibition depends on the degree of aeration, increasing with the latter until a certain level is reached, at which aeration has practically no effect. Hence the proposed distinction between 'inhibition level' (I.L.) and 'complete inhibition level' (C.I.L.). The former affords protection under limited access of air and depends upon the specific degree of aeration, while the latter is a constant for each medium and independent of the degree of aeration.
2. Calcium hydroxide solutions of pH 12 and above afford complete inhibition to mild steel.
3. In mortars and concretes of good quality under usual exposure conditions a pH level of ≥ 12.0 is maintained, affording complete inhibition to reinforcement (in the absence of salts).
4. Sodium chloride and sea salt render steel highly vulnerable to corrosion. Present in small quantities they increase the rate of corrosion, while in large quantities they restrain it. It should be borne in mind, however, that in either case, when present in environments with pH close to inhibition level, they intensify pitting.
5. In the absence of oxygen, or in environments with very high pH , no adverse effect of salts was found.
6. The alkalinity of air-exposed mortars and concretes containing sea salt is below the inhibition level required for protecting the reinforcement. Hence, no reinforced concrete should be made with sea water and precautions should be taken to prevent the penetration of sea salt (spray or otherwise) into structures, unless permanently immersed in water.
7. In the complete absence of oxygen, a concrete extract containing sea salt afforded practically complete protection to steel at pH 10.3.

The alkalinity of concrete being more than adequate, the concrete would protect the steel completely even when made with sea water – were it not for the fact that no concrete in practice is free of oxygen, some being found dissolved in the mixing water and some in the air liable to penetrate even the very dense concretes.

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WOOD AND PLASTICS*

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ABSTRACT

A comparison between wood products and plastics shows important advantages of the latter, which consist of better homogeneity, in several superior physical properties, of which the most important is dimensional stability. The quality standards of the plastic products and their decreasing cost are important factors influencing current improvements in quality and diversification of wood products and in better utilisation of wood waste.

The link between wood and plastics is twofold: 1) Plastics are incorporated in wood in the form of adhesives, surface coatings, finishes or bulking agents at a steadily increasing extent; 2) Further important developments are taking place in the production of plastics from wood waste and wood components.

The number of variables involved in the use of plastics in wood is large. The recognition of these variables and of the possibilities of producing 'tailor-made' products is a most significant trend in the woodworking industry. The development of new plastic adhesives, of improvements in glues by blending several resins, of more efficient manufacturing processes and of a wider range of products is reviewed.

The possibilities of the use of resins or monomers for improving resistance of wood and wood products to biological attack, to fire and for dimensional stabilisation is receiving increasing attention. Crosslinking of the cellulose in the cell walls or depositing various 'bulking' agents in the 'cavities' of the amorphous regions of the cellulose might result in highly improved wood. Another possibility is the chemical and physico-chemical modification of the components of the middle lamella, the lignin, pentosans or polyuronides, so as to produce water impermeable membranes around the single cells.

Another potentially important link between plastics and wood lies in the use of nuclear radiations. The possibilities are: Easier polymerisation of monomers impregnated on wood; grafting polymers on wood and improvement and simplification of the processes for curing the resin adhesives. The limiting factors for the use of nuclear radiation are the degradation of the cellulose occurring at doses of 1 megarep and the high cost of radiation sources, their installation and shielding at the present juncture.

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1. INTRODUCTION

Wood and plastics present two groups of materials widely differing in their properties. The differences start already with the mode of their formation. While plastics are entirely man-made and may be engineered from a relatively small number of basic molecules to a wide variety of materials with predetermined properties according to their end use, wood is produced by nature, its characteristics are defined *a priori* in its growth period, and vary greatly according to species, growth conditions and age. The most important difference between plastics and wood is the heterogeneity of the wood structure as compared with the homogeneous plastic masses.

The low waste level in the manufacture of plastic products as against the high percentage of waste experienced in the woodworking industries and the high mechanical strength figures of the plastic products at a relatively low density are further important advantages of the plastics.

In Table I a comparison of some of the mechanical properties of wood, wood base materials and plastics is presented (1). It can be seen that the tensile strength and compressive strength of the wood products in the direction perpendicular to the grain as well as the hardness are inferior to those of the plastics. The homogeneity, dimensional stability, ease of molding and dyeing of the latter present further distinct advantages over wood.

Although in the first period after the appearance of the plastic products on the world markets their relatively high price did not enable a successful competition with the cheaper wood products, their superior characteristics enabled them gradually to penetrate into many uses in fields in which wood was formerly exclusively used. This penetration caused a progressive decrease in the price of plastics, with a consequent potential endangering of further markets for wood products.

The general ratio of prices of wood and plastics has recently been quoted at 3.5 to 5 (1). It is to be expected that the price of plastics will gradually decrease, mainly owing to the mass-production methods employed in their manufacture and its far-reaching rationalisation.

The development of the plastics industry brought about a new and specialised range of specifications and presented the woodworking industries with the problem of achievement of new products with improved properties which would enable them to compete favourably with the products of the plastic industry.

In order to achieve better products from wood, work had to be done to eliminate in a far-reaching way the naturally inherent deficiencies of wood, the most important of which are: Susceptibility to biological attack, to insects and fungi, inflammability, lack of dimensional stability, natural defects in the grain of wood, susceptibility to weathering agents and to chemicals. On the other hand, the cost of production had to be lowered, primarily by utilising an increasing percentage of the waste wood.

It is not surprising that the plastic products, owing to their versatility and adaptability, have had the greatest impact on the developments in both the above directions.

The incorporation of plastics in the construction of woodworking materials,

either in the form of adhesives, surface coating, finishes or bulking agents, has expanded greatly the range of wood products on the one hand and brought about improved properties of these products on the other. The modifications brought about in the wood products through the application of plastics are developing in two main directions: applications of the plastic resins on the surface, as in wood-wood laminates or in paper-wood laminates, and application of the monomeric materials to the bulk of the wood material and polymerisation *in situ*, inside the structure of the wood.

The link between plastics and wood is, however, not confined to the introduction of plastics into wood. More and more attention is concentrated on the production of plastics from wood waste and from the chemical components of the wood. To the large family of cellulosic plastics derived from wood, the lignin plastics and the resins based on the wood extractives are slowly added, thus opening new avenues for the utilisation of waste wood materials.

2. PLASTIC RESINS IN THE WOOD PRODUCTS INDUSTRY

The products prepared with the aid of plastic resins deposited on the surface of the wood material now cover an ever-widening field. Starting with the oldest technique of substituting nails by plastic glues in jointing wood assemblies and furniture, production of laminated lumber and timbers, to the production of particle board at various degrees of compression, veneers and plywood, construction of layer wood stock from small pieces, of laminates from wood, paper, plastics and metal, up to wood products finished and coated with plastic resins.

Each of these various applications demands plastic glues of specific properties suitable or even specially tailored to the particular use by the particular process. The adaptation of a glue demands a thorough analysis of the factors involved. The factors concerned with the wood products, such as the nature of raw materials — pH, density, extractives, moisture content, bark content, size of material; factors involving the desired specifications of the finished wood product, such as physical properties, size, conditions of service and cost; factors involving processing conditions, discontinuous or continuous operations, wet or dry methods in the case of boards. The factors involving the resin characteristics to be considered are: durability; cost; storage life; dilutability; retention and precipitability; ease of distribution; bonding efficiency; cure-flow relations under use conditions; colour and odour; smoothness of surface; flexibility and acidity. Finally, the factors involving resin manufacture are of considerable importance; nature and number of primary chemicals; ratio and concentration of reactants; solvent composition; types and ratio of catalyst and modifiers; time-temperature processing cycle, and others (2).

The number of variables and combinations of variables is thus large, and provided they are correctly evaluated by suitable testing methods, will permit an ever-increasing number of products to be manufactured with predetermined properties and service uses from resins specifically prepared for them. The recognition of such variables and of the possibilities of producing 'tailor-made' products is perhaps the most

Comparison of properties of wood, woodworking materials and plastics

TABLE I

	Dimension	Solid wood		Particle Board		Fibre board		Wood Laminates		Thermo-plastics		Phenol Formal
		Pine	Beech	Beech with veneer	Insulation	Hard-board		PVC	Poly-ethylene			
Specific gravity	g/cm ³	0.52	0.72	0.61-0.64	0.70	0.25-0.40	1.10	1.3-1.5	1.38	0.92	1.3	
Water uptake (after 24 hrs. in water)	%	—	—	18	16	50-100	20	0.15-1.5	0.01	—	0.1	
Tensile strength: parallel perpendicular	kg/cm ²	1040 40	1350 70	110	210	15-30	250	800	570	160	500	
Compressive strength: parallel perpendicular	kg/cm ²	550 50	620 100	90-100	180	—	—	—	800	—	800	
Bending strength	kg/cm ²	600-800	800-1000	190-240	430	20-50	450	1200-1900	1100	130	130	850
Impact bending strength	cmkg/cm ²	50	85	—	—	—	13	10	130	—	15	
Hardness (⊥ to grain)	kg/cm ²	150	300	—	—	100	400	2500-4500	1000	—	1000	
Modulus of elasticity	kg/cm ²	120000	160000	—	—	—	33000	100000	30000	1000	30000	

significant trend in the woodworking industry and it may be expected that important further developments in processing equipment, in the nature of the plastic resins, as well as in the range of the products manufactured will occur in the near future.

Some perceptible changes are recently taking place in the wood products industry.

In the field of plywood, the application of synthetic resin adhesives is predominantly practised, and lately a clear trend of increasing the quality of the products by using exterior type adhesives even for plywood intended for interior and limited serviceability conditions has become pronounced. This trend has brought about the increased use of phenolic resins, which are highly water and weather resistant as compared with the urea type adhesives (3,4).

A similar trend is observed in the case of particle board. Most of the particle board produced up to now was intended for use in the interior applications, such as core stock for furniture and millwork and therefore the generally used urea resins were sufficient for the purpose. Lately, however, the production of more resistant types intended for housing applications or even more severe service is gaining ground. The particle board production is thus slowly raising its quality standards, and in addition to the use of more adhesives, particular attention is paid to the possible addition of preservatives and fire retardants to the resins. Another recent development is in the veneer overlaid particle boards, which in addition to their better serviceability allow of more decorative panels to be produced.

The incorporation of plastic glues in the production of hardboards is another interesting and promising development. The water absorption, durability, as well as the strength properties of the hardboards are considerably improved. Laminated hardboards of a density of 1.35 were prepared by incorporating melamine-formaldehyde adhesive sheets between plys of hardboard sheets (5).

The use of lower grade and small piece timber is receiving increasing attention. The possibility of compensating for the low quality of wood by combining it with plastic resins and obtaining products even superior to the solid wood has now been recognized.

An example of such a possibility is laminating two-by-four inch studs from one-by-two inch material (6). Other examples for edge and glued lumber include door jams, window and door rails and stiles and architectural trim. The further development of this important trend of wood waste utilisation depends on evolving new, low cost, fast setting and durable plastic glues, requiring simple processing as well as the mechanization of the procedure for handling and arranging the small wood pieces into the desired forms and sizes prior to glueing.

Further developments with respect to paper overlaid lumber and plywood and sandwich panels will also depend on the availability of suitable plastic glues. Overlays of paper with synthetic resin enable a far-reaching improvement of the surface properties of wood products, yielding durable, smooth, defect free and easily paintable surfaces. The paper overlay restrains greatly the swelling of the lumber core across the grain. Paper overlaid lumber can also be manufactured from low-

quality lumber by edge glueing to the desired size and then glueing on the paper skins. The glueing of such laminates as well as of the paper sheets into the honeycombs of the new sandwich panels with paper-honeycomb cores, and of the plywood or hardboard skins to the cores, will demand high speed continuous glueing operations and highly durable glues, if the production of these new products is to expand.

3. RECENT DEVELOPMENTS IN WOOD-ADHESIVE SYNTHETIC RESINS

It is evident that the range of products obtainable from wood and plastic resins is practically unlimited. These products are actually only nominally wood products. Their properties are determined to a larger extent by the plastics incorporated than by the wood. Research into the production of new synthetic resins and the design of new adhesive and coating formulations is therefore continuing in many directions. Some of the developments in the important branches of the synthetic resins during the years 1956-1959 are reported in the following.

a. Fundamental principles of adhesion

An adhesive bond in wood to wood is composed essentially of the five following primary links:

1. The cohesive strength of the first wood adherent, which depends greatly on the surface texture of the wood.
2. The adhesive bond between the adhesive film and the wood which again depends on the surface texture of the wood in addition to the macromolecular properties of the adhesive.
3. The cohesive strength of the adhesive film itself.
4. The adhesive bond of the other film surface to the wood.
5. The cohesive strength of the other wood adherent.

The basic studies on adhesion were mainly concerned with the properties of the adhesives themselves and dealt with the 2nd, 3rd and 4th links, as can be seen from the excellent summary of the basic principles underlying adhesion both from the thermodynamic and molecular point of view presented by Mark at the Seventh Meeting of the Wood Chemistry Panel (7). Lately, however, more interest has been devoted to the 1st and 5th links, especially in view of the need to find "universal" adhesives which could be used for glueing wood to metal, glass, etc. (8). Further research in this direction might result in better characterization of the properties of the glues in relation to the adherents. It is clear that links 2, 3 and 4 should be only somewhat stronger than 1 and 5, in order that failure should occur in the wood and not in the glue line. The characterization of links 1 and 5 will thus enable the choice of a suitable glue with links 2, 3 and 4 correspondingly higher than the cohesive strength of the adherends, which may be of different wood species as well as of other materials.

b. Phenolic resin

The introduction of the phenolic resins into interior wood products has created a continued and expanded interest in these resins. New phenolic resins and the reduction of glue line costs by the introduction of new extenders were studied (3). The use of phenolic film glues, enabling the elimination of mixing and spreading and the preparation of less compressed panels and thus lowering the cost of glueing was further studied.

Crude phenols, mixtures of phenol, cresol, tricresol and xylenol condensed with formaldehyde have been tried as plywood glues (9).

Condensation polymers of phenolic compounds with polyhydric phosphorus compounds like tetrakis (hydroxymethyl) phosphonium chloride were described as suitable for surface coatings and varnishes with high resistance. According to the time of condensation a range of products from clear, molten, viscous, water and ethanol soluble liquids up to dark brittle solids can be obtained (10).

Cold hardening adhesives were prepared from phenol and formaldehyde by incorporation in the mixture of ethylene glycol and polyethylene glycols (11). Hardening agents, comprising the Al, Ni or Co salts of acetoacetic esters, were suggested for lowering the temperature and shortening the time of hardening of phenol formaldehyde systems (12).

Dicyandiamide-phenol-aldehyde varnishes were prepared in the presence of an alkylolamine catalyst and with the addition of 2-10% by weight of refractory solids. Layers of paper impregnated with 53% of this composition were consolidated at a pressure of 1200 lb/sq.in. at 145°C. The laminates were resistant up to temperatures of 230°C (13).

A condensation product of bisphenol [2,2-bis(4-hydroxyphenyl) propane] with furfural in alkaline solution was described. The product may be hardened by weak bases or mineral acids and can be used for coating and impregnation. It was suggested that furfurylidene groups bridge the position O to the phenolic OH groups to build a double chain (14).

A resin useful in varnishes, coatings and as reinforcing agent in cellulose ester lacquers was prepared from hydroxymethylfurfural on reacting with paratoluene-sulfonamide at pH 10.5 (15).

A plywood adhesive formulation of phenol formaldehyde resins with an average molecular weight of 40,000-50,000 with sodium silicate or with the sodium hydroxide and SiO₂ components was described. The role of the excess sodium hydroxide was to homogenize the mixture and improve the bond strength (16).

Copolymers of phenol formaldehyde with terpenes formed hard tough adherent films on metals when dissolved in toluene and mixed with an equal amount of Neoprene AC (17).

A marked acceleration of the rate of curing of phenolaldehyde resins was achieved by the addition of 2-7% sodium phenolate to the alkaline resin condensate of 60-90%

solid content. The product was described as having good pot life and storage stability (18).

The use of the hydrochloric acid catalysed phenol resin of a high formaldehyde content for films on bare wood and paper surfaces was recently suggested. These films have a poor adhesion to fillers, paints and varnishes and therefore serve as primary sole finishes, having excellent hardness, abrasion resistance, gloss and resistance to solvents, fats, oils and most chemicals (19).

A formulation of phenol formaldehyde, resin, organosiloxanes and linseed oil heated until tack-free, was used as an outdoor coating for wood panels. The varnish applied from a mineral spirit solution was found to be highly weather resistant (20).

A formulation for the use of phenol formaldehyde in the bonding of metals, wood and plastics in aircrafts comprises the glueing of the surface with the liquid resin on which pulverised polyvinylformate is spread as plasticiser. The curing is performed at 140–145°C, 7–14 kg/cm² pressure for 15–20 minutes (21).

Naphthalene formaldehyde resins obtained in the presence of sulphuric acid were found to have a higher light fastness, water resistance, alkali resistance and a higher penetration value than novolak phenolic resins. They are recommended for use as furniture varnish (22).

The improvement of the physical properties of resins from alkyl phenols and formaldehyde when used on paper laminates is achieved by the addition of phenethylphenols and phenisopropylphenols (23).

The gradual addition of dichlorophenols during the condensation reaction of phenol with formaldehyde produces resins with a smaller amount of acetone extractable material. They are less viscous and cure under milder conditions to give laminates of high hardness and mechanical strength. Paper sheets impregnated with this solution, pressed into laminates and cured for 30 minutes at 138°C were self-extinguishing and non-punking when ignited (24).

Polymeric materials suitable as laminating agents, adhesives and film forming agents were prepared from alkoxybenzenedicarboxylic acids. The general formula given for these materials is $(RO)_n C_6 H_3 (COOR') (COOR'')$ in which R is an alkyl radical of 1–4 carbon atoms, R' a vinyl or allyl radical and R'' is H or a vinyl or allyl radical (25).

Work has continued on the copolymerisation of resorcinol and phenol with formaldehyde (4), in order to achieve durable glued products for exterior laminates at a lower cost than the conventional resorcinol resins.

c. Aminoplasts

New formulations of urea glues were developed for use under specific plant conditions and for specific types of wood products. These glues are used not only for cold press and hot press production of plywood, but also in the splicing of veneers, the edge glueing of lumber core stock, and the assembly of flush doors for interior service.

Rose (26) reported on a new high solid liquid urea resin with a separate lubricated

catalyst, which is reported to be replacing conventional powdered tapeless splicer adhesives for the splicing of veneers in several plants. This formulation is said to be cheaper than the powdered adhesive.

The addition of polyhydroxy alcohols, such as xylitol, during the condensation of urea formaldehyde resins was found to increase the stability in storage, the mechanical strength and the water resistance of the adhesives obtained (27).

The esterification of urea formaldehyde alkaline precondensate with butanol in water emulsion is described as yielding clear hydrocarbon soluble resins, suitable for moulding, lacquers and paints (28).

Water and alcohol soluble compositions, useful for spraying the surfaces of wood and cardboard, were obtained by mixing the aqueous alcoholic solution of a urea formaldehyde condensation product with that of a phenol formaldehyde condensation product (29).

Addition of dicyandiamide and urea in equal amounts to formaldehyde and condensation at pH 7 was found to yield stable syrupy prepolymers (30).

Modification of a urea formaldehyde condensate with 5–20% of melamine formaldehyde catalysed by ammonium chloride or sulphate was found to increase the water resistance of the plywoods glued by this composition as compared with urea formaldehyde (31).

The application of urea formaldehyde resins in the form of a water suspension instead of a solution was recently suggested. Heating a urea condensation product at 100°C can be controlled so as to render it water insoluble. Dispersions of 27% and 38% of the product in water were prepared which could be readily spread and produced joints of good dry strength and moderate water resistance. The adhesive prepared in this way was more economical than the usual formulations (32).

New modified triazine resin varnishes have been developed for coating paper. The papers are dry and non-blocking and can be easily laminated in a single low pressure operation to the surface of hardboards, particle boards, veneer plywood, lumber core plywood and fancy face veneer-surface boards, in conventional plywood presses (33). The new triazine resins, the formulations of which were not disclosed, are basically melamines in which molecular modifications were introduced to achieve higher flexibility and dimensional stability.

An adhesive composition of 75–86% of urea and 10–20% of melamine formaldehyde with 1–2% ammonium fluoro-silicate or borofluoride as hardener and a small amount of a metallic soap was suggested for the use in edge glueing of wooden elements. When cured in a high frequency electric splicer, a uniform and completely cured bond was obtained when the clamped pieces were fed through the splicer at 60 ft/min and 149°C (34).

The above formulation is one of a series of glues that are recently being developed for efficient edge glueing. The edge and end glueing is of considerable importance, since it allows to use up the short length of the relatively high grade material in an efficient way. End glueing must be a fast operation so as to achieve economical

production. The glue must be relatively easily applied and spread in order to be suitable for the various qualities of end-grain wood surfaces which are often not machined to the best glueing surface (35). If the glued longer end pieces are to compete with solid lumber, fast setting, strong, low-cost, and durable glue lines are required.

Internal plasticisation of melamine resins was achieved by the condensation of aralkylguanamine with melamine and formaldehyde. The composition, when used in lamination of alpha cellulose sheets, kraft paper and crepe paper, gives improved flexibility (36).

A water resistant starch resin composition was prepared from starch with a urea formaldehyde condensation product, ammonium chloride and a sodium salt of hydrolyzed polyacrylonitrile. The resin adhesive prepared in the form of an aqueous solution containing 20% starch was a heavy, spreadable material with improved tack (37).

d. Rubber base cements

A representative member of this group of adhesives is neoprene rubber dissolved in organic solvents. These adhesives were intended for bonding plastic laminates to wood or wood base materials for counter tops and furniture tops. They are at present used to a limited extent in the glueing of interior type flush doors and for on-the-job installations of plywood panelling to wall framing members (4, 38). The adhesives are applied to both surfaces, dried either in air or infrared dryers to a tack-free condition, and pressed cold or while still warm from the infrared drying under low pressure for a short time.

Curing plays a very small part here and the action seems to depend rather on physical phenomena concerned with the high initial cohesive strength of the adhesive film.

One of the main difficulties with these adhesives is the inflammability and toxicity of the vapours of the organic solvents in which the neoprene cements are dissolved and applied. The assessment of the point of complete removal of the solvent presents some difficulties. Furthermore, the relatively low stability of the adhesive solutions and the rather low strength of the joints produced by them indicate that much further study is required to adapt them to further applications in the woodworking industry.

One development in the direction of obviating the inflammability and toxicity hazards was the recent introduction of water emulsions of the rubber cements. These emulsions are also potentially less expensive than the organic solvent type adhesives.

An important new use of the neoprene cements is for bonding thin veneer flooring to concrete slabs in house construction instead of rubber asphalt and tile floors laid directly over the concrete slabs.

New formulations based on bitumens derived from petroleum, which have been bleached by solvent extraction or by acid treatment and are suitable for fastening wooden structures to cement, plastics, cork, ceramic materials and in cementing

wood mosaics and parquets was recently described (39). These formulations contain 50% bleached bitumen, 35% water, alkyds, melamines or phenol-formaldehydes, latex, potassium oleate and lithopone.

An adhesive for bonding of wood, rubber, glass and metal based on polybutadiene reacted with hydrogen peroxide and formic acid in chloroform was described (40).

Polymers of cyclopentadiene and its copolymers with linseed oil in the presence of tin tetrachloride gave films of good adhesion and stability to ultraviolet light and water. They remained elastic, hard and strong in interior and exterior applications (41).

Polymerisation of cyclopentadiene with styrene, indene or coumarone and with unsaturated fatty acids and their derivatives yielded coating type resins, light-coloured, light stable, fast drying and having good adhesion to wood and metals. They can be applied from solutions of xylene, toluene and benzene (42).

e. Polyvinyl base resins

The polyvinyl resins are usually applied in the form of solutions in organic solvents or as water emulsions. While their application is simple and the addition of hardeners is not required, their slight abrasion resistance, their reversibility and the insufficient water stability of their films greatly restrict their use (43).

The polyvinyl resins are used for glueing plastic laminates to plywood cores for table and desk tops and in cold press bonding of flush doors in short pressing cycles.

Instead of the addition of external plasticisers for improving the durability of the polyvinyl resins, more attention is recently being paid to the preparation of their copolymers with urea or phenolic resins in order to provide an internally plasticised resin. The urea formaldehyde and polyvinyl acetate copolymer gives somewhat greater water resistance, better performance and provides freedom from the undesirable creep characteristics of the polyvinyl acetate, while retaining its quick-setting properties.

Coatings resistant to chlorinated organic solvents, glacial acetic acid, concentrated nitric acid and alkali were prepared from hydrolyzed copolymers of vinyl chloride, vinyl acetate or vinyl alcohol with furfural. The copolymer does not cross-link when protected from air and light. It is applied in thin films to wood or metals and crosslinks by air catalysis (44).

Upgrading of the properties of polyvinylchloride resins was obtained by their chlorination with gaseous chlorine in tetrachloroethane solution at 130°C (45).

Copolymers of vinylacetate, ethyl acrylate, alkali metal or ammonium acrylate in aqueous emulsion were found to be suitable adhesives for bonding vinyl resins to wood, bamboo and paper (46). Another composition suggests a mixture of vinyl acetate chloride, a mineral spirit solution of acrylic ester-styrene-drying oil copolymer and isophorone. The mixture is emulsified in water containing morpholine. After addition of plaster of Paris and wood flour the product is suitable for coating or filling of wood (47).

Emulsions of polybutenes, consisting essentially of homologous branched chain hydrocarbons, were suggested as extenders in polyvinylacetate coatings in the manufacture of fibreboards, soundproof insulation boards and in paints (48).

By copolymerisation of vinyl chloride and vinyl acetate and saponification of about 70% of the free OH groups, a heavy polar film-forming material is prepared (49). Such polymers are suitable as base coats on wood and cardboard for water emulsion coatings with vinyl resins as compounding agents. The copolymers are dissolved in a mixture of methanol and acetone and the solution is applied to the articles to be treated. As soon as the solvent evaporates the water emulsion is applied.

Vinyl ethers containing quaternary ammonium groups were lately suggested for use in the manufacture of adhesives, lacquers and coatings (50). From a mixture of 2-diethylaminoethyl vinyl ether and chloroacetoamide after heating in a boiling water bath and dissolving the resinous mass obtained in water, the quaternary compound $(\text{CH}_2:\text{CHOCH}_2\text{CH}_2\text{N}(\text{Et}_2)\text{CH}_2\text{CONH}_2)\text{Cl}$ is obtained. When epichlorohydrin is substituted for chloro-acetoamide the corresponding compound $[\text{CH}_2:\text{CHOCH}_2\text{CH}_2\text{N}(\text{Et}_2)\text{CH}_2\text{CH}(\text{CH}_2)]\text{Cl}$ was obtained.



Styrene and butyl acrylate were emulsified with these compounds in the presence of tris (hydroxyethyl)dodecylammonium acetate and isooctyl alcohol in water. The emulsion was further polymerised by stirring and heating with potassium persulphate.

Quaternized polymers of a vinyl heterocyclic N compound of the pyridine or quinoline series were described as bonding agents for laminating metals and wood. One such formulation comprises a copolymer of butadiene, 2-methyl-5-vinylpyridine mixed with a commercial mixture of dichloropropanes. The products are set at high pressure of 2,000 lbs/sq.in. and 150°C (51).

f. Acrylic resins

Reacting of urea, formaldehyde and acrylonitrile in concentrated sulphuric acid solution, neutralizing with sodium hydroxide, distillation, and recrystallisation from ethanol, yielded acrylamidomethyleneurea (52). If, instead of urea, melamine is used, the polymerisable melaninemonomethyleneacrylamide is obtained (53). Instead of acrylonitrile, nitriles of α,β -unsaturated carboxyl acids of the general formula $\text{CH}_2:\text{C}(\text{R})\text{CN}$, where R is H, Cl or an alkyl radical, could be used. The aqueous solutions of these compounds can be polymerised by addition of catalysts and may be used for adhesives and lacquers (54).

The copolymerisation products of hydroxymethyl melamines and acrylonitrile were also prepared by emulsion polymerisation in the presence of potassium persulphate (55). The copolymer products were described as elastic and rubberlike materials, completely insoluble in solvents such as benzene.

Mixtures of phenol formaldehyde resins with a rubbery butadiene-acrylonitrile copolymer and a filler were described as adhesives for plywood (56).

A series of latex emulsions were produced from acrylonitrile or styrene butyl acrylate and ethyl acrylate or 2-hydroxyethylmethacrylate by blending with phenol-, urea- or melamine- formaldehyde condensation products. These emulsions, when dried and baked as coatings on wood, produced hard, glossy films, resistant to solvents and chemicals (57).

Esters of acrylic and methacrylic acids, when polymerised in the presence of carboxylic anhydrides (benzoic, acetic, trichloroacetic) and amine oxides (*p*-toluidine oxide, tribenzylamine oxide) yielded hard and clear resins useful in coating, laminates, as impregnates and adhesives (58).

A new type of adhesives, the *cyanoacrylates*, attracted much attention recently. The alkyl, cyclohexyl and phenyl-cyano-acrylates of the general formula $\text{CH}_2\text{:}-\text{C}(\text{CN})\text{COOR}$ were used. These polymers are substantially anhydrous and are prepared with formaldehyde, methanol or other organic solvents, which distil below the depolymerisation temperature of the polymer. After completing the reaction, part of the solvent is distilled off. Benzene, capable of forming an azeotrope with water, is added. Further distillation allows the lowering of the water content to 0.4%, which is necessary for storage stability.

The product is dried with P_2O_5 and hydroquinone and depolymerised by heating in a stream of SO_2 (59). Heating the methyl, ethyl or cyclohexyl- α -cyanoacrylates in closed containers for 72 hours at 65°C in the presence of 0.002% SO_2 and 0.05% hydroquinone causes no polymerisation but increases the stability of the product (60).

The bonding of these polymers to acidic surfaces, like green wood, phenolic resins or bonded plywood, is catalysed by moistening with a monohydroxy alcohol containing 1–8 carbon atoms (61). The alcohol is thought to remove the polymerisation inhibitors present, but does not give too rapid sets.

The cyanoacrylates form high strength adhesives for bonding glass, metals, plastics, wood, paper, cloth, cement, to each other or to themselves (62). They are 100% reactive and fast setting at room temperature by the action of slight amounts of moisture present in the air and in the adherents.

g. Epoxy resins

The interest in using epoxy resin formulations in the woodworking industry has lately been growing despite their rather high cost. Their ability to adhere to many surfaces, such as plastics, glass and metals, their curing at room temperature without the liberation of volatile byproducts and solvents, and their 100% reactivity, will enable them to be introduced into the production sequences of a number of special wood products (63).

The major consideration limiting their wider use is their price. The inclusion of alkenes in resins prepared from glycidyl ether (obtained from polyhydric phenols with epichlorohydrin) with amines of fatty acids as curing agents was recently described. The addition of the alkene lowers the cost, reduces the viscosity and improves the temperature stability and toughness of the resin (64).

Epoxy resin, cured with multivalent metal salts of enolketo tautomers like Al, Ni, Co and Cu salts of acetoacetic acid ester, malonic ester and formylacetone were found to give improved stability in storage. The glueing of the surfaces coated with the fluid resin is carried out at 120°C without pressure (65).

Diepoxy thermosetting compositions of a wide viscosity range, yielding fire resistant adhesives, were obtained from diglycidyl phthalate treated with sebacic or adipic acids or with 1.5-pentanediol and combined with chlorinated phthalic anhydride (66).

Another similar composition which is described as being particularly suitable as adhesive coating and varnish for wood is prepared from glycidyl ethers with polyfunctional acid anhydrides, like phthalic and dichlorophthalic anhydrides, sebacic acid and a tertiary amine like dimethylbenzylamine. The mixture is cured at 65-130°C and has excellent impact resistance, insulation resistance, adhesion and a low dielectric constant (67).

One of the most important properties of the epoxy resins is their compatibility with other synthetic resins. Their toughness and high adhesive properties single them out as upgrading agents for coatings of many types. The resulting composite formulations which are actual reaction products rather than blends, possess properties surpassing those of the single resins. The addition of a butyl alcohol solution of a phenolformaldehyde resol to a solution of diglycidyl ether in diacetone alcohol and xylene at 120°C results in a resin suitable for coatings possessing excellent resistance to alkalis, boiling water and organic solvents and high flexibility and impact strength (68, 69).

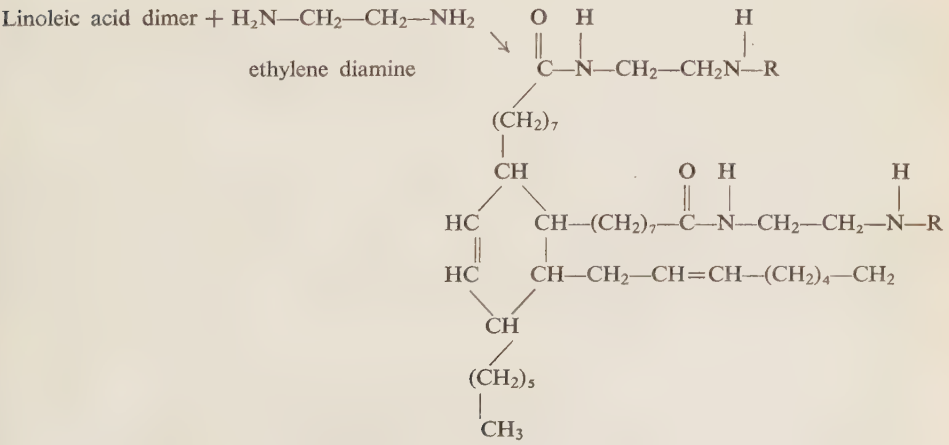
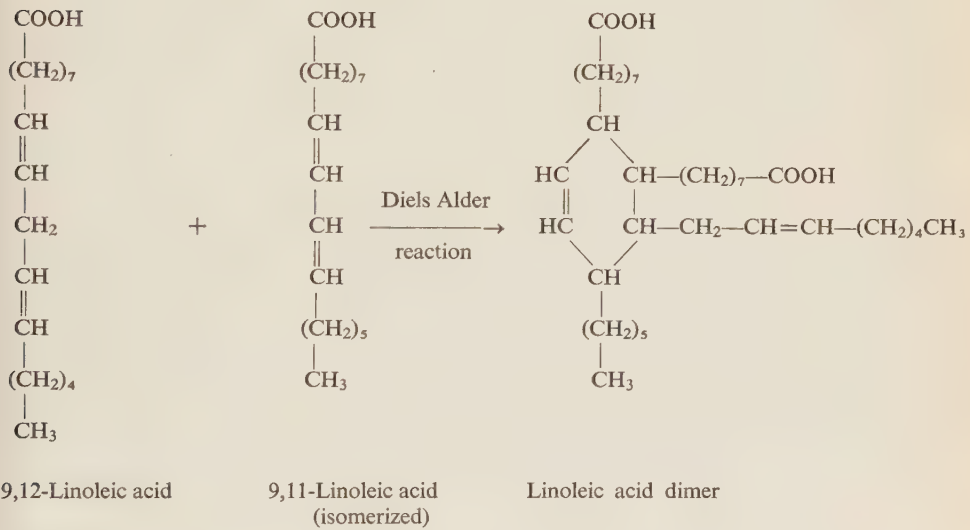
Incorporation of polyamide resins into the epoxy resin formulations has a particularly marked modifying influence on the latter. The replacement of the amines in the amineepoxy resins by polyamide offers both a curing agent and a modifying resin. The advantages gained are as follows:

- 1) Less critical ratios of components;
- 2) Less exothermic reaction and longer pot life;
- 3) Elimination of toxicity effects;
- 4) Less moisture sensitivity, and
- 5) Higher gloss and better flexibility (70, 71).

The optimum ratio of polyamide to epoxy resin will depend on the specific application. Higher percentages of polyamide will improve peel strengths; lower percentages will permit retention of adhesive bonds at somewhat higher temperatures. The higher the amount of polyamides, the more flexible will be the bond. A film of polyamide epoxy resin cures in 3 minutes at 205°C. Blends of equal parts of polyamide and epoxy resins can be made without solvent by adding the polyamide heated to 60°C to the room temperature fluid epoxy resin.

The polyamide resins used for these reactions are condensation polymers of dimerized and trimerized vegetable oil, unsaturated fatty acids and aryl or alkyl polyamines

(72). An approximated structure of these polyamides is presented below, in which R may be another linoleic acid dimer group. The free amine groups remaining in the condensed resin serve as additional points for epoxy crosslinking and catalytic polymerisation. The high concentration of the polar groups is responsible for the outstanding adhesive properties. The high flexibility is imparted by the presence of the aliphatic polyamide chains which separate the rigid benzene rings of the epoxy molecules and provide for a greater degree of freedom for the chains to assume under stresses and impact loadings (73).



The use of epoxy resins, modified with primary and condensed polyamines or with polyisocyanates for the preparation of paints and enamels was recently discussed by Nedly (74). These cold curing films possess superior characteristics with respect to durability, adhesion and chemical and mechanical resistance of the thermosetting types. Their high price and toxicity during application prevent a more general use at present.

h. Other resins

The preparation of condensation products from unsaturated aldehydes or ketones with polyhydroxy alcohols for their use in varnishes and adhesives was described. Azodiisobutyronitril was condensed under nitrogen with diallylidene-pentaerythritol. The products obtained were colourless powders, soluble in a number of organic solvents. They contain free double bonds and can be melted when carefully heated (75).

A furniture glue can be prepared from a new product prepared from a condensation product of cyanuric acid with formaldehyde (76).

A novel catalyst-buffer procedure for converting intermediate stage furfuryl alcohol condensation products used as adhesives and molding compositions to hard coherent resins was recently disclosed. The furfuryl alcohol is treated with dilute nitric acid and formaldehyde. The condensation product obtained is dissolved in a mixture of acetone and methylethylketone and mixed with a solution of alkylbenzenesulphonic acid. Upon the addition of a small amount of benzidine (2%) or aluminium triacetate the mixture was permanently set at 20°C in 30 minutes. The product was applied in laminating wooden billets by coating one surface with the ketone solution of the condensation product mixed with benzidine and coating the second surface with the aqueous solution of the sulphonic acid. The surfaces were clamped at 150 lb/sq.in. for 20 minutes. The laminates obtained gave a shear test of 2,500-3,000 lb/sq.in. (77).

Reaction products of hydantoins with formaldehyde were suggested for impregnation of paper to increase the wet tear strength (78).

Hexahydrodimethylaniline and Fe-acetylacetonate have been described as foaming accelerators when applied as prime coatings for foamed polyurethanes used in the adhesion of sheet metals or plywood (79). The foaming of glues prior to spreading facilitates the control of glue spreads uniformly, at low weight and consequently low cost. Phenol formaldehyde and urea formaldehyde resins are used in conjunction with chemical stabilisers of the foam (80).

It was stated to be possible to spread urea resins uniformly at a rate of only 15 pounds per 100 square feet of single glue line by use of the ordinary glue spreaders and the chemical foaming technique. The use of foamed resins is of great interest for the future development of wood-plastics products, but much has yet to be done in improving the glueing technique, the spreading equipment and the introduction of better formulations of these resins.

Film forming materials, useful for coating floors, tables, walls etc. were prepared from neutral or acid esters of malonic acid with monohydric alcohols in the presence of sulphuric acid, or p-toluenesulphonic acid, as catalysts. The resulting crosslinked

malonic acid polyesters are soft, rubbery, tacky products which may be mixed with large amounts of fillers (81).

i. The ideal glue

The search for better and lower-cost synthetic glues is continuing at an increasing pace as is evidenced by the large number of papers and patent specifications published in recent years. It is not to be expected that an 'ideal' glue suitable for the whole diversified range of wood-plastic products will emerge. It seems likely that future developments will continue in the direction of 'tailoring' glues from the known plastic materials to the specific requirements of any given product. The increasing demands in higher quality will require adhesives of more stringent specifications, higher durability and easier applicability. Much more is to be learned on the fundamentals of adhesion and on the interrelation between the adhesives and adherends before exact predictions as to the performance and adaptation of an adhesive to a given product can be made.

An attractive development might be the combining of the action of the adhesive formulation with specific reactivities of the wood components. Such a concept has recently been brought forward by Blomquist (82), on discussing glues for fast setting operations in which the necessity of heating the gluelines should preferably be avoided. A glue with a long pot life but rapid curing in the assembled joint under low pressure and at room temperature would be required for this purpose. This could be achieved by a latent chemical 'trigger' device in the resin, such as a special catalyst system which would be activated rapidly by rapid withdrawal of a retarding component into the wood through a chemical interaction with one of the wood components.

4. IMPROVING RESISTANCE OF WOOD AND WOOD PRODUCTS TO BIOLOGICAL ATTACK AND TO FIRE BY USE OF PLASTICS

The possibility that application of plastic resins to wood products might improve their resistance to biological attack and to fire has attracted some attention in recent years. Buro (83) investigated the influence of several acidic and alkaline formulations of urea and phenol-formaldehyde resins impregnated on wood on the rate of growth of *Coniophora cerebella*, *Lentinus lepideus* and *Polystictus versicolor*. While the phenol-formaldehyde resin did not influence the rate of growth of the above fungi there was a marked inhibition of growth rate in the presence of the urea-formaldehyde resins. Investigation of the influence of the amount of resin, the molar ratio of the precondensate and the degree of hardening of the resins pointed to the conclusion that the degree of growth inhibition increases with the increase in volatile and water soluble constituents of the resin.

While phenol-formaldehyde resins were found not to influence the resistance of wood fungi, some protection against the action of termites was obtained on laminated

multilayer plywood glued with phenol-formaldehyde resin, when their surface was completely coated with the resin (84).

A modified phenol-formaldehyde resin obtained by the gradual addition of mixed dichlorophenols to the phenol and formaldehyde mixture during the reaction was found to impart fire resistant properties when applied for paper lamination (24).

Another resin applied for flameproofing wood products was prepared from amine salts of meta- or pyrophosphoric acid mixed with condensate of melamine and formaldehyde (85). Fibreboard soaked in the aqueous solution of this resin dried at 70°C and hardened at 140°C was found not to support burning and did not glow.

A similar product was obtained from mixtures of meta-, pyro-, or polyphosphoric acid with condensation products containing methylene-imine ($\text{HN}:\text{CH}_2$) groups, like guanidine or dicyandiamide in an aqueous acid solution. Fibreboards prepared from pulps beaten with the above mixture and pressed at 150°C were found to be highly resistant to flames and had excellent mechanical properties (86).

While the above phosphoric acid containing resins are applied in aqueous solution on the whole of the fibreboard material, several new resin formulations were described which are coated on the fibreboard or wood. In one such formulation sodium silicate, a rubbery polymer of a butadiene hydrocarbon and acrylonitrile together with a high percentage of an insulating refractory are mixed in water to form a tacky workable dispersion. Thin coating with this dispersion protects wood for some time even at temperatures of 2200°C, along with showing good impact resistance and very little cracking (87).

In another formulation fibreboard or accoustical tile is coated with an intumescent coating of a carbohydrate and a film forming polymer latex (88). On this coating an additional outer coating is applied, consisting of equal amounts of polymer latex and urea-formaldehyde resin. This fire resistant coating was found to be stable in washing.

5. PLASTICS AND ADHESIVES FROM WOOD COMPONENTS

Another interesting link between wood and plastics is concerned with the use of wood or of the chemical components of wood for the production of plastics and adhesives, either by themselves or after chemical modification or condensation with various synthetic monomers.

The main wood component which has continued to attract the most attention in this respect is the lignin which still constitutes a waste fraction of the wood in the pulping operation. The purpose of the series of papers and patents published recently was to find uses for the lignin, either in its isolated forms, as chloro-lignin or lignosulphonic acids, or of the sulphite waste liquors.

The preparation of synthetic resins from lignin and acetylene was recently described by Nikitin *et al.* (89). The reaction is carried out either with lignin or kraft black liquor containing 5% sodium hydroxide or with CO_2 precipitated dry lignin dissolved in 5% NaOH in a revolving autoclave at an initial pressure of 13–14 atmospheres

and a temperature range of 150—170°C, the acetylene being fed stepwise. The resin obtained after 40—50 hours of interaction with a yield of 190% based on the original lignin had a melting point range of 60—90° and formed transparent films which adhered to glass, metal and wood.

A similar resin was obtained when the reaction was performed with guaiacol instead of lignin. It seems likely that the acetylene reacts with the free hydroxyl groups of the lignin, giving monomeric units of the following type $\text{Ph}(\text{OMe})(\text{OCH}=\text{CH}_2)$. These units polymerise further to form the resin.

An intermediate product for the production of synthetic resins from lignosulphonic acid of sulphite waste liquors by heating with amino acids at temperatures between 40–100°C and acidifying was described by Trumpler (90).

A plastic resin was obtained from chlorolignin and phthalic anhydride in methanol solution upon refluxing and evaporating (91). When applying a mixture of this resin with phenol and formaldehyde, heated with an alkaline or acidic catalyst and dried under reduced pressure to wood, the absorbed resin is hardened to give highly strengthened wood.

Resins suitable as paints for metals were obtained by condensation of acetophenone, cyclohexanone or methylcyclohexanone with lignin and humic acids. The reaction occurs between the carboxyl groups of the ketones and the active methylene groups of the lignin (92).

A moulding composition was obtained (93) by reacting lignin with lignosulphonic acid in the presence of fluoboric or dihydroxyfluoric acid. The action of the halogen acids is presumably the decrease of the polymerisation of the lignosulphonic acid. Phosphoric, phthalic and sulphuric acid esters are added as plasticisers and the mixture is moulded after keeping for 45 minutes at 60–70°C.

A similar moulding composition of dried and fine grained lignin and lignosulphonic acid at a ratio of 10:1 was obtained on heating them with 9% furfural containing 20% of phenol or cresol and a small amount of phosphoric or phthalic acid esters or plasticisers (94). The mixture, after preheating at 60°C, was moulded by pressing at 120–125°C at a pressure of 300 kg/cm². The moulds obtained according to this process are claimed to be resistant to chemical agents, water repellent, lustrous, and to have the high mechanical strength of 1000 kg/cm².

Another interesting moulding composition from lignin obtained as a byproduct in the manufacture of vanillin from sulphite waste liquor (95) was recently described. The lignin used in this composition is a desulphonated lignin obtained on centrifuging of the concentrated sulphite waste liquor after heating with alkali at 165°C and acidifying to pH 4–4.5. The desulphonated lignin is heated with sulphuric acid, washed with water and dried. It constitutes 45% of the moulding powder, the other components of which are: wood flour (45%), hexamine (6%), ochre (3%), and oleic acid (1%). The moulded lignoplast was shown to have 68% of the impact resistance, 34% of the hardness, 114% of the heat resistance and approximately the same di-

electric properties of a standard phenol-formaldehyde mould while the cost of the new mould was only 50% as compared to the standard mould.

Several processes in which lignin was condensed with phenols to form plastic materials have been described.

A condensation product of decationised sulphite waste liquor with a relatively small amount of phenol when treated with aldehydes yields a thermosetting binder suitable for the consolidation of sawdust and shavings into fibreboards and plywood corestock (96).

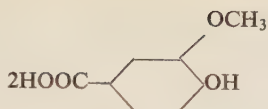
Lignin obtained from low temperature hydrolysis of wood with 40% HCl was reacted with about 30% phenol at 136°C in the presence of acidic catalysts (97). The low viscosity reaction product obtained is further condensed with hexoses and pentoses prepared from mother liquor of the wood saccharification process, under the addition of formaldehyde, to yield a thermosetting resin at a relatively low cost.

The conversion of another byproduct of wood hydrolysis, the lignin-carbohydrate to a plastic material has also been suggested (98). The lignin-carbohydrate is kneaded at 120°C with 12% of its weight of hexamethylene-tetramine and 80% of ground wood filler in the presence of benzene. After distilling off the benzene, the resulting powder is press-moulded at 190°C to give hard thermosetting products.

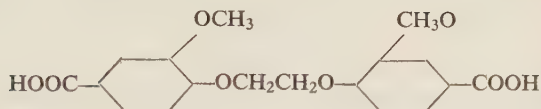
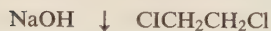
The use of lignosulphonic acid or their reaction products with anhydro-formaldehyde-aniline or phenol alcohols for the increase in the rate of hardening of urea-melamine-formaldehyde resins has been suggested (99).

The preparation of resins for the impregnation of paper laminates from xylenol extracted lignin and formaldehyde was investigated by Farkas (100). The lignin was extracted from pine sawdust in the presence of concentrated sulphuric acid as catalyst. The extracted lignin which contained some xylenol was condensed with formaldehyde by solution in hot alkali and refluxing for one hour at 55°C. The lignin-xylenol-formaldehyde resin was precipitated from the dilute solution by neutralizing with sulphuric acid and regulating the pH to 4.5 with aluminium sulphate. The resin was found to be applicable by a wet method — mixing the alkaline solution of the resin with the pulp fibres and precipitating on the fibres — or by a dry method — first precipitating and grinding the resin and then mixing with the pulp. The electrical insulation and mechanical properties (with the exception of tear) of the paper laminates obtained when pressing the sheets at 150°C and 95 kg/cm² were good and it was suggested to use the resin in place of phenol-formaldehyde resins for the production of paper laminates.

Bock and Anderson investigated the possibility of preparing synthetic polymers from vanillic acid, which is potentially available from lignin and is bifunctional, containing a carboxyl group and a phenolic hydroxy group (101). The vanillic acid was first converted to dibasic acids by etherifying the phenolic hydroxyl groups by reaction with alkylene dihalides.

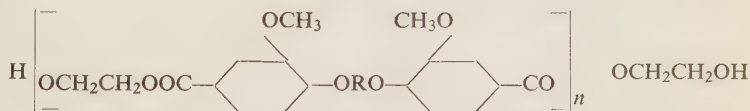


Vanillic acid



1,2 bis(2-methoxy-4-carboxyphenoxy)ethane

The dibasic acid was further esterified with ethylene glycol to form the bishydroxyethyl ester of the dibasic acid. The esters were condensed to linear polyesters by heating in the absence of oxygen to 275°C:



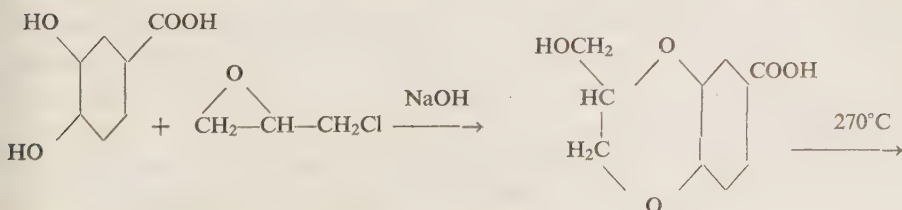
Polyester from vanillic acid

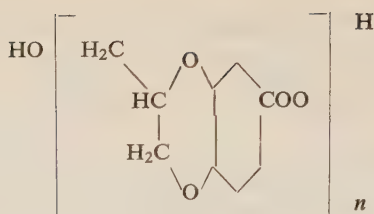
R = alkylene group

The polyesters were converted by melt spinning to fibres which could be stretched in a warm water bath, to give fibres with good tenacity and increased crystallinity. Owing to its lack of symmetry this polymer has a melting point of 200°C but a softening point of only 80°C.

In order to obtain a polymer of a more rigid structure these authors investigated the preparation of a cyclic derivative from protocatechuic acid, which can be obtained by the alkaline fusion of lignin.

Both phenolic hydroxyl groups of protocatechuic acid were etherized by reacting with epichlorohydrin in the presence of sodium hydroxide to form a 1,4 benzodioxan derivative which contains one primary hydroxyl group and one carboxyl group:





6 (or 7) Carboxy-2-hydroxymethyl-1,4-benzodioxan and polyester.

This hydroxyacid was condensed by heating in vacuum to form a linear polyester which was converted to fibres by melt spinning. Relatively high tenacity fibres of 4.4 g per denier and melting point of 210°C and a high softening point of 145°C were obtained.

The possibility of directly utilising the distillate obtained from the steam hydrolysis of acid impregnated oak wood chips for the production of resins curable with aldehydes and suitable for moulding, rubber compounding and bonding glass fibres was described (102). The solution containing 2% of 5-hydroxymethyl-2-furaldehyde is mixed with 2% phenol, refluxed at an alkaline pH for 50 minutes and the resin obtained is precipitated with acid at pH 2.

Several investigations on the use of wood and bark extracts in the preparation of resins and plastics were published. Ramos (103, 104) reported on the preparation of the monophenoxyacetic acid dibenzyl ether from the catechol tannins of the Peruvian pashaca, mangrove and quebracho barks and from pashaca wood. This compound is obtained by reacting the extracts with chloroacetic acid, yielding the sodium phenoxy acetate of the tannin and by subsequent reacting with benzyl chloride in alkaline solution and acidifying. Upon addition of formaldehyde water insoluble resins were obtained.

A detailed study on the preparation and uses of tannin-aldehyde resins for bonding of particle board and glueing of veneers was carried out in these laboratories. The influence of the production variables of plywood on the properties of the glue line with particular emphasis on the durability was studied in detail (105).

Narayanamurti *et al.* (106) studied the preparation of adhesives from tannins in the bark of the *brugiera* species. Marian and Wissing (107) studied the utilisation of polyphenols from spruce bark for the preparation of adhesives.

The relatively low price of the bark polyphenols and the relative ease of preparation from some plastic adhesive components combined with their high durability (105) which is similar to the phenol-formaldehyde adhesive shows encouraging prospects for the future utilisation of waste barks in many countries. The wide variation, however, in the properties of the extracts from the barks of various origins call for further detailed studies.

It is noteworthy that the hemicellulose fraction of the wood comprising the pentosans and polyuronides and constituting 15–30% of the wood or plant material

which is partly or wholly wasted in the pulping operations has attracted only little attention. The main utilisation of this fraction for the production of plastics seems to be via the furfural and its derivatives obtained by distillation of the pentosans. The relatively complicated structure of the hemicelluloses and their variability in the different plant species demands further basic study before useful and well-defined products could be produced from them.

6. MOULDED WOOD PRODUCTS

The moulded wood products are finding utilisation in an increasing number of commodities like toilet seats, wooden bowls, shoe heels and table legs. The moulds are prepared from sawdust or defibred wood by applying a suitably prepared resin with particular flow properties and low degree of condensation.

While in the case of plywood and wood or wood paper laminates or when glueing lumber the action of the adhesive is confined mainly to the surface, in the case of wood moulds the resin applied penetrated deeper into the wood structure owing to the high surface area of the comminuted wood used in the preparation of the mould. These preparations naturally require a higher percentage of resin and thus out of all composite wood plastic products they are closest to plastics. In the following several recent developments in moulded wood products are reviewed.

Sheets were prepared from sawdust previously cooked with 2% NaOH at 140°C, cooled, mixed with 20% cork flour and 10% dry phenol-formaldehyde resin and pressed at approximately 10 kg/cm² at 160°C. These sheets are usable in furniture, wall panels, doors, etc. (108).

A similar product has been obtained by applying to pine chips previously compressed at 800 kg/cm² 30% of their weight of a urea adhesive, and moulding at 90°C with high frequency heating (109).

Sawdust or defibred cornstalks, bagasse, mechanical pulp or shredded newspapers were converted to dense, hard and smooth surfaced moulded articles such as table tops by first mixing with urea and drying, and thereafter mixing with acidified furfural and pressing in plated press moulds at 135°C (110).

Dense, water resistant fibreboards were produced by continuous feeding of defibred wood and a phenol-formaldehyde resin, followed by partial drying and uniform felting onto a moving wire screen (111).

Mixtures of phenol-formaldehyde polycondensate and polymerisate with urea formaldehyde and at least 50% of sulphonaphthenic acids were used in preparing moulds from wood waste (112).

Wood fibre laminated articles of high shock resistance and high surface hardness were made by using more resin on the surface layers than in the cores. The composition of the outer layer consisted of 65% phenolic resin, 3% of a copolymer of 1,3-butadiene and acrylonitrile and 32% wood fibre while that of the core consisted of 30%, 5% and 65% of the respective components (113).

An interesting recent development in the field of moulded wood products was

the appearance of the flapreg or flakeboards (114). The flapregs belong to the impreg-compreg materials and are based on the formation of an insoluble thermosetting resin within the cell structure. The resin, in the form of a low molecular weight condensate, usually phenol-formaldehyde, is allowed to diffuse into the wood. The water is evaporated at moderate temperatures and then the material is cured at suitably high temperatures to polymerise the resin. One of the important considerations in the manufacture of these products was the achievement of considerable dimensional stability and reduction in hygroscopicity.

In the manufacture of impreg, the impregnated veneers were dried, cured, glued up and then pressed in the manner of plywood. This material is of moderate density, good dimensional stability, high tensile and flexural strength, high water resistance and needs only small amounts of lacquer for finishing (115).

In the case of compreg the impregnated and dried veneers are glued up in the uncured condition and pressed at high pressure and temperature. It has a high density (1.4 g/cm^3), very low water absorption and high strength, particularly compressive strength.

In the case of flapreg instead of veneer thin wood flakes of average dimensions of $0.008 \times \frac{1}{4} \times \frac{1}{2}$ inches are used. The flakes can be prepared inexpensively from any solid wood residue and adapted to completely mechanised handling, similar to usual particle boards. Thus, while being similar in properties to compreg as evidenced in Table 2 (114), it can be produced at a much lower cost. The size of the flakes enables rapid resin penetration by spraying in a rotary drum mixer for 10–15 minutes.

TABLE II
Physical Properties of Flapreg and Impreg

Douglas fir flapreg (Random orientation)				
	No. of tests	Minimum	Maximum	Average
Specific gravity	8	1.39	1.39	1.39
Modulus of rupture (psi)	8	12,100	13,700	13,170
Modulus of elasticity (psi)	8	1,690,000	2,140,000	1,910,000
Internal bond (psi)	6	912	1,188	1,097
Thickness swell % 24-hour water soak	8	0.2	0.8	0.42
Water absorption % 24-hour water soak	8	0.41	0.50	0.44
Sitka spruce compreg (cross laminated)				
Specific gravity	8	1.32	1.36	1.34
Modulus of rupture (psi)	8	14,610	16,360	15,240
Modulus of elasticity (psi)	8	2,262,000	2,343,000	2,290,000
Internal bond (psi)	—	—	—	—
Thickness swell % 24-hour water soak	—	—	—	—
Water absorption % 24-hour water soak	6	1.41	1.54	1.46

35% solid resins on the basis of the dry flakes are applied. This high amount of phenol formaldehyde enables to eliminate fairly completely the air void and fill the intracellular voids of the obtained product, so that in pressing at a limiting density, approaching 1.4, the compressibility of the board drops to near zero.

The flakes are dried to 0–5% moisture before spraying and to 5% after spraying. In the machine felting a mat thickness of about 8 inches is necessary per inch of finished board. The pressing and curing is done at 700–2000 psi at 148°C for 15–25 minutes.

The flāpreg is resistant to acids and organic solvents and is attacked only slowly by strong alkali. It is practically cigarette-burn proof.

Flāpreg in board or sheet form was suggested for the manufacture of table counters and furniture tops, cutting boards, shelves, floor tiles, wall panelling and electrical insulation. Machined in final form, it might be used in gears, electrical parts, cutlery handles, golf club heads, brush handles and other items.

7. IMPROVING WOOD BY CROSS-LINKING AND POLYMERISATION IN SITU

As mentioned above, one of the main deficiencies of wood and wood products, as compared to plastics, is the lack of dimensional stability. Imparting dimensional stability to wood would greatly improve the quality of wood products and bring it closer to the standards of plastics. Research in this direction is being presently expanded and several new developments have been recently reported upon.

The changes in the dimensions of wood are caused by the changes in moisture content of the wood products with changes in the relative humidity of the air or on wetting. The wood fibres swell on absorbing moisture and this swelling causes strains in the internal wood structure which are transferred to the external dimensions, causing warping, twisting and shrinking of the wood, thus reducing its serviceability and decreasing its useful life-span.

The moisture absorption in the wood fibres occurs at the hydrophilic hydroxyl groups of the non-crystalline parts of the cellulose. The non-crystalline or amorphous regions of the fibres are not unequivocally defined and little is known on the actual arrangement of the cellulose chains in them. The possibility exists that several kinds of amorphous cellulose exist in a single wood fibre. These regions are considered to be penetrable to water or dyestuffs and yet not enough information is available on the actual size of the 'pores' in which this penetration occurs. The chains in the amorphous region are considered to be randomly arranged at varying angles and consequently varying distances exist between different segments of neighbouring molecules. The cavities thus occurring between the molecules may be of widely varying dimensions. The water molecules will accumulate in these cavities and cause their expansion until restrained by elastic stresses of the cellulose chains extending from the 'cavity' into more ordered regions where they are more strongly held together. This restraint brings about an equilibrium moisture condition.

Increasing the dimensional stability of wood could be obtained by one of the following possibilities:

1. Closing up the whole structure from moisture so that no outside influence could change the moisture content inside the given wood product. This is one of the primary aims of the wood finishes and coatings. These treatments, however, only retard the penetration of moisture into the structure but do not bring about a stabilisation of the moisture content.

2. A mechanical partial curbing action on swelling and shrinking can be obtained by adhesives in the case of plywood and by paper overlays in the paper wood laminates.

3. Diminishing the volume of the cavities by causing crosslinking of the cellulose chains with suitable crosslinking agents. Investigations in this direction were recently summarised (116, 117) and much attention has been given to crosslinking with formaldehyde in which methylene bridges are introduced between hydroxyl groups of adjacent cellulose molecules. The addition of 0.5% formaldehyde of the weight of the wood was reported to reduce the shrinkage of wood by 60%. The short methylene bridges are, however, too rigid and the wood is embrittled. In addition, during the treatment the cellulose is noticeably degraded by the acidic catalyst.

Other agents investigated are acrylonitrile, acrolein and lately acrylamide and polyacrylamide. In the cyanoethylation of the cellulose with acrylonitrile not only reduction in swelling of wood by 75% and diminishing the equilibrium moisture content of the wood is achieved, but in addition the wood is stabilized against biological attack.

The acrolein reacts with the wood through the aldehyde group and through the double bond and its application in vapour phase might be possible.

The advantage of acrylamide over acrylonitrile and acrolein consists chiefly in its relatively low toxicity. Water soluble poly-acrylamides could be impregnated in the wood. Acrylamide and polyacrylamide, can be reacted with formaldehyde to produce methylolacrylamide, containing reactive groups which could crosslink with either itself or with the hydroxyl groups of the cellulose.

4. Instead of diminishing the volume of the 'cavities' by crosslinking, they could be filled with bulking agents, which would combine with the hydroxyl groups of the cellulose and possibly also partly produce crosslinking. A considerable number of chemicals has been tried out as bulking agents; acetylation, alkylation and acylation, treatment with beta-propiolactone, or with ethylene glycol. The impregnation with resins, as in the case of impreg, compreg and flapreg, also belongs to this category. The bulking treatments are, however, limited by the considerable amounts of chemicals needed, which consequently render their cost prohibitive. If low cost small molecular size bulking agents could be applied in such a way as not to degrade the cellulose and in simple processes, the problem of the dimensional stabilization of wood would approach its solution.

5. Another way of dimensionally stabilising wood might be the formation of thin films around the cellwalls which would hinder the penetration of moisture into the cell. Such a film would act as a mechanical barrier applied on the single fibre. This might be achieved by reacting the components of the middle lamella. The swelling inhibition of lignocellulosic materials by the lignin in the middle lamella is well known (118). The depression of the swelling by the lignin has been attributed to two main reasons: firstly, the small moisture absorption of the lignin, which does not support the transmission of water molecules; secondly, there is a possibility that at least in certain cases a part of the lignin exists in the lignocellulosic material in the form of a three-dimensional network surrounding the cells and acting as a mechanical barrier to the penetration of water (118, 119).

If the lignin could receive an additional crosslinking treatment *in situ*, so as to render it completely impermeable, it would act as a stable impermeable coating on each single fibre. Specific reactants with good penetrability would have to be applied for such a process. The amounts of such reactants needed would have to be small and only minor changes would occur in the properties of the wood since the fibres themselves would remain intact.

A similar possibility could be conceived with the hemicelluloses of the middle lamella. The pentosans or polyuronides could be crosslinked by specific reagents at reaction conditions that would be based on the possible differences between the reaction rates and reactivities of the amorphous cellulose in the secondary wall and the hemicellulose in the true or compound middle lamella. A possibility of strengthening the lignin-carbohydrate complex in the middle lamella by introducing further chemical links between them might lead to a similar result. On the other hand, the hemicellulose-alphacellulose complex (120, 121), the existence of which in several wood species was lately suggested, could also possibly be built up by selective reactions in such way as to bring about marked changes in the moisture relationships of the wood.

Before any of these possibilities could be accomplished, much more is to be known on the composition, structure and properties of the middle lamella and its components, on the state in which these components exist in the wood, and on their reactivity and diffusibility, as compared with the cellulose in the cell wall.

8. NUCLEAR RADIATION—A NEW POTENTIAL LINK BETWEEN WOOD AND PLASTICS

The recent developments in the study of applications of nuclear radiation in the field of polymers open new and interesting possibilities for: a) improving the properties of wood and wood products by enabling easier polymerisation and crosslinking of monomers impregnated on wood; b) grafting polymers on wood; and c) simplifying the process for curing of resin adhesives in wood products.

The possibility of carrying out polymerisations in the wood structure by neutron or gamma ray radiations might be attractive. The radiation might replace in such

reactions the necessary catalysts; the reaction might be carried out at low temperatures; the rate of the reactions could be rapid. The doses of radiation needed in polymerisation are low, since the action of radiation is mainly to start the chain reaction. If a reaction of the type of crosslinking wood cellulose with formaldehyde could be carried out by nuclear radiation, the degradative influence of the acidic catalyst needed in the conventional reaction would be eliminated.

Of even greater interest might be the grafting of polymers on wood. Such a process might result in highly improved properties of the wood products, by combining the physical properties of the wood with those of the grafted polymer. On irradiation of wood impregnated with acrylonitrile, grafting occurred which gave a product with highly improved strength and lowered moisture absorption and swelling (122). On the other hand, however, irradiation of birchwood dowels, after soaking in methylmethacrylate monomers, yielded the incorporation of 30% polymer in the wood as a bulking agent that did not change greatly the values of the equilibrium water content or of the swelling, but diminished the rate of the attainment of the equilibrium water content (123).

Another potential use of nuclear radiation in the woodworking field might be the increase in the rate of curing of synthetic resins or the enhancement of their adhesive properties. The curing of styrene-polyester systems with high velocity electrons from a van de Graaf accelerator was done in 10 seconds, as compared with 3-15 minutes for cures with the conventional peroxide catalyst. While the peroxide catalysts shorten the pot life by accelerated gelation, in the case of radiation induced curing inhibitors could be added which did not interfere with the curing (124).

The adhesive properties of polyethylene film to glass and paper have been greatly improved by irradiation. A dose of 10^7 reps of gamma radiation increased the force required to tear the paper from a polyethylene and paper laminate five-fold (125). The curing of adhesives of the polyester, natural rubber and synthetic rubber types by application of high velocity electrons without raising the temperature has been suggested (126).

The use of nuclear radiation in the woodworking industries is, however, limited by the degradative action on the cellulose. It is known that cellulose is very susceptible to radiation damage at levels exceeding 10^6 reps. The degradative changes consist in depolymerisation of the cellulose, increase in carbonyl and carboxyl groups, increase in water and alkali solubility and decrease in tensile strength (127, 128, 129). Any reaction with wood would therefore have to be limited to low radiation doses. The doses necessary for polymerisation of monomers are in the range of 0.2-5 megareps (130). The rates of polymerisation of different monomers at the same radiation dose rates depend on the nature of the monomer.

The polymerisation of butadiene at a dose rate of 900 reps/sec proceeds at a rate of 0.01 % per hour, while vinyl acetate emulsion polymerises at a rate of 27 % per hour (131). While the radiation induced degradation of cellulose was found to be independent of the dose rate (132) it is evident that the total doses of radiation used will

have to be limited and therefore only polymerisations requiring a low total dose will be possible with wood. A similar consideration applies to the grafting on wood. Here the radiation dose required is from 1–2 megareps, but rapid cases in which only 0.05–0.1 megareps are needed, are known.

Another important limitation to the application of nuclear radiations in the wood-working industries is the cost factor. Even if the doses of radiation needed will not be prohibitive, the investment in the radiation sources, their installation and shielding are rather high. For the treatment of solid thick lumber high intensity sources will be necessary, producing radiation of high penetrability and wide enough scan. It seems likely that the first applications of nuclear radiation will be in the field of fibreboard and particle board or wood-resin laminates, in which resin could be polymerised, or copolymerised in sheets passing continuously through exposed tunnels. Unless far-reaching quality improvements are obtained by the radiation curing the cost will have to compete with conventional methods. Such comparisons in the field of wood products have not yet been made.

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LETTERS TO THE EDITOR

Heat and mass transfer on the surfaces of cold liquids

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The present note is intended to draw attention to a problem of obvious practical importance which so far does not seem to have been adequately investigated: the condensation of moisture from the atmosphere on the surface of open chilled water or brine tanks such as used e.g. in ice and ice-cream plants.

The mass transfer problem looks comparatively simple. With the surface substantially below the dew point of the air, condensation will occur at the rate¹

$$m'' = (h/c_p)(\delta/\alpha)(\Delta P/P) = h(\Delta P)/2210 \quad (1)$$

The real difficulty is the determination of the heat transfer coefficient h between the air and the cold surface. Downward heat transfer has been very scarcely investigated in the past, and it is doubtful how far existing data, which seem to be based on tests with rather small surfaces², can be applied to practical cases of large tanks. Obviously the convection mechanism between a cold surface and warmer air above cannot be simply interpreted as a 180° reversal of the heating process above a horizontal plate.

However, in order to obtain at least a reasonable approximation, a sample calculation has been carried out on the basis of the classical equation³

$$h = 1.13(\Delta t)^{0.25} \quad (2)$$

The total heat transferred will include both the latent heat of the condensed vapour and the sensible heat

$$q'' = m''r + h(\Delta t) = 597m'' + 1.13(\Delta t)^{1.25} \quad (3)$$

Results are shown in Figure 1 for assumed outside air of 60% relative humidity and a constant surface temperature of 0°C. The latter value is, of course, higher than the brine temperature of an ice freezing tank, but since most of the exposed surface is actually water in the moulds, the assumed value will be reasonably near the average.

It will be obvious that the figures obtained cannot be neglected in a sub-tropical climate. Figure 1 shows for 25°C a heat transfer of just over 150 kcal/m²h equivalent to an extra load of about 0.1 kW for every square meter of tank surface. Expressed differently, a bath 1 m deep will tend to grow warmer by 1° every 7 hours. Moreover,

the condensation of about 150 g/m²h water means a continuous weakening of the brine concentration which would work out at about 1% (absolute) every three days. In practice, night temperatures will be substantially lower, thus reducing those influences, and tanks are usually covered for a considerable part of the working time, but the figures computed are certainly large enough to warrant further investigation.

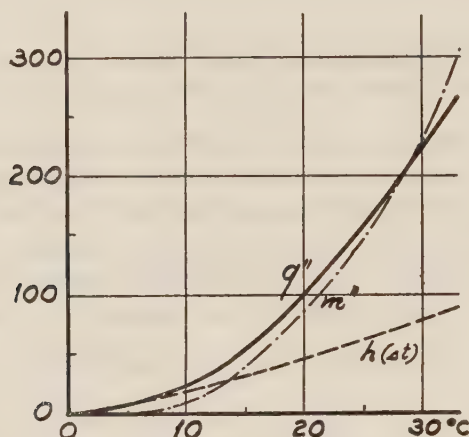


Figure 1

Heat and mass transfer from air at 60% relative humidity to freezing water at 0°C.

Abscissa: Air temperature.

Ordinates: — — — $h(\Delta t)$ = sensible heat transfer, kcal/m²h
 - . - . - . m'' = quantity of vapour condensed, g/m²h
 ————— q'' = total heat transfer, kcal/m²h

Symbols:

m'' = water vapour condensed, kg/m²h (in Figure 1: g/m²h)
 h = film coefficient for heat transfer from air to water, kcal/m²hC
 c_p = specific heat of air = 0.24 kcal/kgC
 δ/α = air/water diffusion ratio = 1.09
 ΔP = difference between vapour pressure in the air and that corresponding to the surface temperature, kg/m²
 P = barometric pressure, here 10⁴ kg/m²
 Δt = temperature difference between air and surface, °C
 q'' = total heat transferred, kcal/m²h
 r = latent heat of water vapour at 0°C = 597 kcal/kg.

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Thiamine destruction as an index of soymeal heat treatment

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The extent of heat treatment to which soymeal has been subjected can be followed by determining changes in thiamine content.

Seven samples of solvent extracted soybean meal were tested and the results are summarized in Table I.

TABLE I
Thiamine content of soybean meal

No.	Description of meal	Thiamine content (mcg/g)
1	Optimally heated	3.7
2	Overheated	1.0
3	Optimally heated	2.1
4	Underheated	6.7
5	Underheated	8.9
6	Raw	13.4
7	Dry toasted	2.5

The wide range of thiamine in the tested samples enables us to distinguish clearly between various stages of heat treatment, especially as the content of the nutrient in the raw beans varies to a small extent: Usually between 10.3 and 10.7 mcgr/g; in extreme cases between 9.6 and 14.6 mcgr/g^{1,2,3}.

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יוצא לאור ע"י

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